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CONTENTS

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Availability of Micronutrients in Gujarat Soils Part II

RESPONSE TO MICRONUTRIENT APPLICATION ON SOME REPRESENTATIVE SOILS OF GUJARAT

R. T. DANGARWALA and B. V. MEHTA

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Introduction

Micronutrients have been found to be either components or activators of the enzyme systems, and as such their deficiencies lead to severe metabolic disturbances which adversely affect the yield and quality of the produce. Deficiency symptoms on plants appear only in extreme cases, but often there is hidden hunger which cannot be detected by visual appearance and still it affects the yield. It appears that there is a considerable scope for improving the yield and quality in the case of high-yielding varieties by including micronutrients in the fertilizer schedule.

This experiment was conducted to study the response of crops to the application of Fe, Mn, Zn, B, Cu and Mo in some of the representative soils of Kaira and Baroda districts of Gujarat where intensive cultivation is practised.

Material and methods

(*a*) Soil selection :

On the basis of soil analysis, soils having values of available micronutrients below the critical level for deficiency as well as those having values above the critical limit were selected, because it was felt that with the introduction of high-yielding varieties there may be a response to

applied micronutrients. Samples were collected from Anand, Boriavi, Borsad, Tarapur, Mehmadabad, Torna and Thasra of Kaira district and Gorwa, Sokhadakhurd, Wankaner and Limda of Baroda District.

(b) Pot-experiments :

The pot-culture study was made in *rabi* season as well as in hot weather. In *rabi* season cauliflower (var. Snowball) was grown as an indicator crop for B, oats (var. Kent) for Mn, wheat (var. S. 227) for Cu and lucerne (alfalfa-var. local) for Mo. In hot weather season, hybrid maize (var. Ganga-5) was grown as an indicator crop for Zn and sorghum (var. CHS-1) for Fe.

Treatments : Three, viz. (1) *Control*, (2) *Soil application* : (*i*) 10 ppm Zn as $ZnSO_4 \cdot 7H_2O$ (*ii*) 0·5 ppm Mo as $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (*iii*) 25 ppm Mn as $MnSO_4 \cdot 4H_2O$ (*iv*) 10 ppm Cu as $CuSO_4 \cdot 5H_2O$ (*v*) 5 ppm B as $Na_2B_4O_7 \cdot 10H_2O$ (*vi*) 10 ppm Fe as $FeSO_4 \cdot 7H_2O$ and (3) *Foliar application* : (*i*) 0·6 % $ZnSO_4$ + 0·3 % $Ca(OH)_2$ (*ii*) 0·05% ammonium molybdate (*iii*) 0·6 % $MnSO_4$ + 0·3 % $Ca(OH)_2$ (*iv*) 0·4 % $CuSO_4$ + 0·2% $Ca(OH)_2$ (*v*) 0·2% borax (*vi*) 0·4 % $FeSO_4$ + 0·2% $Ca(OH)_2$.

Replications : Three

Soil application was done along with the application of basal dose prior to sowing or transplanting. Analar–grade chemicals were used to supply NPK as the basal dose as well as micronutrient application in the soil or on the plant as foliar spray. Foliar spray treatment was given after one month of the establishment of plants.

(c) Pot-culture technique :

The polythelene-lined earthen pots of 4 kg. capacity having 24 cm and 11 cm of upper and lower diameters respectively with a drainage hole at the bottom were used for the experiments. Representative soil was thoroughly mixed with twice the recommended basal dressings of NPK. Only

one half of the N was applied initially and the remaining half after about one month of sowing or transplanting. Throughout the course of experiments the moisture level in the pots was maintained at 80 per cent of field capacity by irrigating regularly with glass-distilled water except in case of B experiment, wherein distilled water from copper distillery was used. The crops were harvested after about 2 to 3 months depending upon the growing stage of the crops. Dry-matter yields were recorded.

(*d*) Analytical technique :

Wet-ashing procedure was employed for estimating Mn, Cu, Zn and Fe in plant material, while dry-ashing was followed for B estimation. Boron was estimated by Hatcher and Wilcox method (1950), Mn by periodate method (Jackson, 1958), Cu by modified method of Cheng and Bray (1953), Zn by Holmes method (1945), and Fe by orthophenanthroline method (Jackson, 1958).

General description of soils

The soils included in pot-studies are locally called *goradu* from their colour and texture. They are alluvial in nature of Indo-Gangetic type. Texture of the soils is sandy, loamy sand or sandy loam. These soils are very deep and have excellent drainage. Physical and chemical characteristics of the soils are given in Table 1.

In general, pH was more or less around neutrality, except that of soils of Boriavi, Borsad and Tarapur which were slightly alkaline. There was practically no salt accumulation.

Organic matter content of soils varied between 0·40 and 1·20 per cent. Soils of Anand and Torna contained least organic matter, while it was highest in Boriavi soil. Total nitrogen content of soils followed almost similar pattern to that of organic matter and ranged from 0·021 per cent in Torna to 0·070 per cent in Boriavi. The C : N ratio varied from 7·2 to 12·3. The soils can be rated as moderate to high in availability of phosphate except Torna soil, which was deficient in phosphorus. Available potash content varied from 11·0 to 28·6 mg. per 100 g soil, indicating sufficiency of potash in all the soils. Cation exchange capacity (C.E.C.) of soils varied from 8·5 to 15·1 m.e. / 100 g soil, excluding Torna, which had a low value of 3·5 m.e. only.

TABLE 1

Physico—chemical Properties of Soils Used in Pot-culture Study

Constituents	*Anand*	*Boriavi*	*Borsad*	*Gorwa*	*Limda*	*Mehmadabad*	*Sokhadakhurd*	*Tarapur*	*Thasra*	*Torna*	*Wankaner*
	1	2	3	4	5	6	7	8	9	10	11
Texture	Loamy sand	Sandy loam	Sandy loam	Sandy loam	Loamy sand	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Sandy	Sandy loam
pH (1 : 2.5)	7.1	7.9	7.8	6.5	7.2	7.2	7.7	7.9	7.0	7.5	7.1
Conductivity mmho/cm (1:1)	0.33	0.61	0.55	0.74	0.50	0.33	0.41	0.63	0.50	0.33	0.50
Organic matter per cent (colorimetric procedure)	0.40	1.20	1.00	0.90	0.55	1.05	0.82	0.77	0.80	0.40	0.57
Organic carbon per cent	0.23	0.70	0.58	0.52	0.32	0.61	0.48	0.45	0.46	0.23	0.33
Total nitrogen per cent (Kjeldahl's digestion method)	0.028	0.070	0.062	0.054	0.041	0.054	0.039	0.051	0.048	0.021	0.046
C : N ratio	8.2	10.0	9.4	9.6	7.8	11.3	12.3	8.8	9.6	11.0	7.2
Available P mg/100 g soil (0.5 M $NaHCO_3$ pH 8.5)	1.1	4.9	3.5	4.8	2.1	2.8	2.0	1.2	5.1	0.2	3.8

	1	2	3	4	5	6	7	8	9	10	11
Available Potash mg/100 g soil (neutral N NH_4OAc)	19.7	24.8	27.8	12.3	13.2	17.4	15.2	28.6	22.2	11.0	14.7
C.E.C. m.eq./100 g soil (neutral N NH_4OAc)	8.9	11.4	15.1	12.9	8.5	9.8	12.6	15.1	10.6	3.5	10.3
Available Fe ppm (1 N NH_4OAc pH 4.8)	8.2	8.0	13.2	13.0	7.5	12.2	15.7	9.5	34.0	6.5	14.5
Exchangeable Mn ppm (neutral N NH_4OAc)	7.1	5.3	4.3	6.2	2.1	8.0	6.7	3.0	10.4	6.2	6.7
Easily reducible Mn including exchangeable Mn ppm (neutral N NH_4OAc+0·2% hydroquinone)	63.0	51.0	67.0	122.0	113.0	75.0	96.0	145.0	86.0	57.0	47.0
Available Zn ppm (neutral N NH_4OAc+0.01% dithizone)	1.14	1.10	2.67	1.75	0.95	3.97	1.14	0.93	1.80	0.54	1.43
Available B ppm (hot—water—soluble)	0.09	0.33	0.57	0.10	0.16	0.19	0.31	0.22	0.31	0.12	0.16
Available Cu ppm (neutral N NH_4OAc)	0.11	0.13	0.41	0.19	0.21	0.63	0.15	0.20	0.13	0.07	0.11
Available Mo ppm (acid ammonium oxalate pH 3.3)	0.051	0.054	0.062	0·072	0.062	0.058	0.047	0.034	0.072	0.021	0.040

None of the soils contained less than 2 ppm of available Fe, below which response is likely. Exchangeable Mn varied from 2.1 to 10.4 ppm, while easily reducible Mn ranged between 47 and 145 ppm. Available *Zn* (dithizone–ammoniumacetate--extractable) varied between 0.54 and 3.97 ppm. Torna soil contained least available *Zn* which was very near the critical limit of 0.50 ppm; hence beneficial effect of *Zn* application may be expected on this soil. Hot-water–soluble B showed a variation of 0.09 to 0.57 ppm. Available B content of Anand, Gorwa and Torna soils was very near the critical limit of 0.1 ppm and they may respond to B fertilization. Minimum available Cu content was 0.07 ppm, while maximum was 0.63 ppm. Available Mo content varied between 0.021 and 0.072 ppm, least being in Torna soil, while it was highest in soils of Gorwa and Thasra.

Results and discussion

(*i*) Boron–cauliflower crop :

None of the plants exhibited any visual deficiency symptoms of B and all plants were normal. Overall statistical analysis of yield data (Table 2) indicated that the treatment differences were not significant

TABLE 2

Effect of B application on the dry matter yield (in g.) of cauliflower

(on oven--dry basis--mean of 3 replications)

Sr. No.	*Village*	*Control*	*Soil application*	*Foliar application*
1	Anand	6.6	7.2	7.8
2	Boriavi	7.6	8.2	8.7
3	Borsad	8.9	10.9	10.9
4	Gorwa	10.3	9.6	7.5
5	Limda	9.4	11.2	7.6
6	Mehmadabad	10.4	8.6	10.0
7	Sokhadakhurd	9.4	9.6	6.9
8	Tarapur	10.3	10.2	12.1
9	Thasra	7.9	7.8	8.7
10	Torna	6.7	5.8	8.3
11	Wankaner	9.1	7.2	9.8
	Mean	8.8	8.8	8.9

	L.S.D. @ 5%	S.Em.	C.V.%
Treatment	N.S.	1,98	24.2
Interaction	2,5	0.87	17.4

but their interaction with the village (soil) was significant. Boron application in the soils of Limda and Sokhadakhurd yielded significantly more than foliar spray application. In Torna and Wankaner soils, reverse was true as foliar spray gave higher yield than soil application. Although such differences among methods of application were obtained, no response was observed to B application on any of these soils. Soil analysis of these soils revealed that only Anand soil containing 0.09 ppm of available B, is likely to respond to B fertilization, but no significant response was observed. It may be stated, however, that there was a tendency for increase in the yield due to B application in this case.

Boron content (Table 3) of cauliflower plant under the control treatment varied between 22.5 and 37.5 ppm. Under soil application and foliar spray treatments it varied from 22.5 to 37.5 and 33.0 to 77.5 ppm respectively. Gandhi and Mehta (1960), working with different plant species, found that leaves of cauliflower contained 75 ppm of B.

TABLE 3

Effect of different methods of B application on B content and its uptake by cauliflower

(mean of 3 replications)

Sr. No.	*Village*	*Control*		*Soil application*		*Foliar application*	
		Plant content (ppm)	*Uptake mg./pot*	*Plant content (ppm)*	*Uptake mg./pot*	*Plant content (ppm)*	*Uptake mg./pot*
1	Anand	36.25	0.24	66.00	0.48	67.50	0.53
2	Boriavi	31.87	0.24	36.25	0.30	38.00	0 33
3	Borsad	42.50	0.38	40.00	0.44	52.50	0.57
4	Gorwa	22.50	0.23	22.50	0.22	36.20	0.27
5	Limda	37.50	0.35	43.70	0.49	51.00	0.39
6	Mehmadabad	36.20	0.38	33.75	0.29	38.70	0.39
7	Sokhadakhurd	27.50	0.26	36.20	0.35	36.20	0.25
8	Tarapur	27.50	0.28	32.50	0.33	40.00	0.48
9	Thasra	31.20	0.25	31.20	0.24	33.00	0.29
10	Torna	30.00	0.20	42.20	0.25	77.50	0.64
11	Wankaner	36.25	0.33	42.50	0.31	52.50	0.52

Berger (1949) reported that tops or roots of healthy vegetable crops such as beans, beets, cabbage, carrots, lettuce, tomato and turnip contained 30 to 40 ppm of B. But he has not given the value for cauliflower. The minimum value obtained was 22.5 ppm in case of Gorwa soil. Since the crop growth was quite healthy in this case and there was no response to B application, it may be said that this content of B in above-ground portion of cauliflower plant, 93 days old, was adequate for B nutrition of cauliflower.

Minimum uptake of 0.20 mg. per 4 kg. soil was recorded in Torna soil of Kapadwanj taluka, while maximum of 0.38 mg. per 4 kg. soil in Borsad and Mehmadabad soils. It ranged from 0.22 to 0.49 mg. per 4 kg. soil under soil application and from 0.25 to 0.64 mg. under spray application. Calculated on hectare basis, minimum uptake of B under control was 112 g. in Torna soil and maximum of 213 g. in Borsad and Mehmadabad soils.

(*ii*) Manganese–oats crop :

All plants were normal and deficiency symptoms of Mn were not observed on any of the plants. Overall statistical analysis of the yield data (Table 4) revealed that neither the treatments nor their interaction

TABLE 4

Effect of Mn application on the dry matter yield (in g.) of oats

(on oven–dry basis–mean of three replications)

Sr. No.	*Village*	*Control*	*Soil application*	*Foliar application*
1	Anand	6.0	6.3	6.4
2	Boriavi	11.1	9.8	10.1
3	Borsad	11.5	10.6	10.7
4	Gorwa	12.0	11.4	11.4
5	Limda	10.0	10.9	10.0
6	Mehmadabad	8.4	9.1	9.1
7	Sokhadakhurd	9.3	10.0	9.4
8	Tarapur	7.1	7.0	7.4
9	Thasra	9.7	8.6	6.9
10	Torna	5.8	5.1	5.5
11	Wankaner	8.6	8.9	8 3
	Mean	9.0	8.9	8.7

	L. S. D. @5 %	S.Em.	C.V.%
Treatment	N.S.	0.17	11.1
Interaction	N.S.	0.60	11.6

effects were significant. However, there was a tendency for a slight increase in the yield in case of villages Limda, Mehmadabad and Sokhadakhurd due to Mn application. No response was observed to Mn application as the availability of soil Mn appeared to be adequate. Soil analysis has shown that the exchangeable Mn content of soils used in the pot-culture study was more than 3 ppm except in Limda soil of Waghodiya taluka in Baroda district, which has 2.1 ppm of exchangeable Mn. But its easily reducible Mn content was 113.0 ppm, indicating sufficient Mn availability to meet the normal requirement of plants for their successful growth.

Under the control treatment, Mn content of oats varied between 36 and 160 ppm (Table 5). Similarly it varied between 50 and 134 ppm under soil application treatment and between 48 and 162 ppm under foliar spray. Thus, minimum Mn content of oats was 36 ppm. Samuel and Piper (1929), Piper (1931) and Leeper (1935) found 14 to 15 ppm in the whole plant at the flowering stage to be the lowest value in healthy cereals. Oats with 7 ppm showed pronounced deficiency symptoms (Nicholas, 1949). Baser and Saxena (1970) found that Mn absorption was higher in legumes as

TABLE 5

Effect of different methods of Mn Application on the Mn content and its uptake by oats

(mean of three replications)

Sr. No.	*Village*	*Control*		*Soil application*		*Foliar application*	
		Plant content (ppm)	*Uptake mg./pot*	*Plant content (ppm)*	*Uptake mg./pot*	*Plant content (ppm)*	*Uptake mg./pot*
1	Anand	160	0.96	134	0.86	162	1.04
2	Boriavi	50	0.56	60	0.59	76	0.77
3	Borsad	44	0.51	54	0.57	70	0.75
4	Gorwa	142	1.70	94	1.07	152	1.73
5	Limda	54	0.54	78	0.85	88	0.88
6	Mehmadabad	36	0.30	50	0.46	48	0.44
7	Sokhadakhurd	36	0.34	60	0.60	60	0.56
8	Tarapur	114	0.81	114	0.80	118	0.87
9	Thasra	82	0.80	88	0.76	120	0.83
10	Torna	82	0.48	98	0.50	108	0.59
11	Wankaner	54	0.46	66	0.59	88	0.73

compared to cereals. Of these cereals, in wheat it ranged between 15 and 85 ppm and in barley it varied from 10 to 60 ppm. The ranges mentioned for these two crops would also hold good for oats. In the present study the least Mn content of oats was 36 ppm under control indicating sufficiency of available Mn in all the soils.

The Mn uptake of oats under control treatment ranged between 0.30 and 1.70 mg. per pot containing 4 kg. soil. Similarly it varied between 0.46 and 1.07 mg. per pot under soil application treatment and between 0.44 and 1.73 mg. per pot under foliar spray. Calculated on hectare basis minimum uptake of Mn from untreated soil was 168g. in Mehmadabad soil and maximum was 952g. in Gorwa soil both of which produced normal crop.

(*iii*) Copper-wheat crop :

The wheat plants grown in pots were all normal and did not show any visual deficiency symptoms. Overall treatment differences were not significant (Table 6). The interaction effect was significant. In case of Gorwa

TABLE 6

Effect of Cu application on the dry matter yield (in g.) of wheat

(on oven-dry basis-mean of three replications)

Sr. No.	*Village*	*Control*	*Soil application*	*Foliar application*
1	Anand	11.5	11.2	10.1
2	Boriavi	18.6	16.1	17.0
3	Borsad	16.8	14.8	13.1
4	Gorwa	15.7	10.7	16.1
5	Limda	13.6	15.1	13.7
6	Mehmadabad	11.1	11.9	11.6
7	Sokhadakhurd	12.8	11.8	13.8
8	Tarapur	11.5	12.5	13.1
9	Thasra	12.5	12.7	12.6
10	Torna	12.5	11.3	12.5
11	Wankaner	13.9	13.8	15.0
	Mean	13.7	12.9	13.7

	L.S.D. @ 5 %	S.Em.	C.V.%
Treatment	N.S.	0.39	16.50
Interaction	2.2	0.78	10.12

soil containing 0.19 ppm of available Cu, foliar spray has yielded significantly more than that receiving Cu through soil application, but in none of the soil the control was significantly less than the soil or foliar treatment. It has been mentioned under soil study that Torna soil containing 0.07 ppm of available Cu, which was below the critical level as per Wood's standard, may respond to Cu application, but statistically no significant response was obtained to Cu application either in the form of foliar spray or as soil application.

Copper content of wheat plants under control varied between 4.5 and 10.0 ppm (Table 7), between 4.0 and 23.5 ppm in plants under soil application and between 38.5 and 59.0 ppm in plants receiving foliar spray.

TABLE 7

Effect of different methods of Cu application on the Cu content and its uptake by wheat

(Mean of three replications)

Sr. No.	*Village*	*Control*		*Soil application*		*Foliar application*	
		Plant content (ppm)	*Uptake mg./pot*	*Plant content (ppm)*	*Uptake mg./pot*	*Plant content (ppm)*	*Uptake mg./pot*
1	Anand	9.0	0.10	6.0	0.07	52.5	0.53
2	Boriavi	5.0	0.09	8.5	0.14	42.0	0.71
3	Borsad	8.5	0.14	9.0	0.13	49.0	0.64
4	Gorwa	6.0	0.09	13.5	0.14	41.5	0.67
5	Limda	9.5	0.13	10.0	0.15	48.0	0.75
6	Mehmadabad	9.5	0.11	16.5	0.20	47.5	0.55
7	Sokhadakhurd	10.0	0.13	23.5	0.28	49.0	0.68
8	Tarapur	9.5	0.11	14.0	0.18	59.0	0.77
9	Torna	4.5	0.06	6.0	0.07	46.0	0.58
10	Thasra	9.0	0.11	10.0	0.13	47.0	0.59
11	Wankaner	9.0	0.13	4.0	0.06	38.5	0.58

Neelkantan and Mehta (1962) reported 15.6 ppm of Cu in normal wheat plants growing under field condition in *goradu* soil of Anand. Greaves and Anderson (1936) reported that healthy wheat plants contained 5.6 to 16.7 ppm of Cu. Joshi and Joshi (1960) stated that wheat seedlings became toxic if they contained more than 10 ppm Cu and the sufficient range was from 5 to 10 ppm. Using sand-culture technique Agarwala *et al.* (1971) found that normal wheat plants of different varieties contained 4.3 to 7.0 ppm Cu, while deficient plant contained 2.2 to 3.8 ppm. Mehta *et al.* (1969), working with different varieties of wheat grown at two locations viz. Anand and Thasra, found a variation of 5.6 to 19.0 ppm of Cu with an average of 11.4 ppm in Anand samples, while in Thasra samples, a range of 5.0 to 22.5 ppm with a mean of 14.7 ppm was obtained. In the present study, Cu contents of wheat plants (control) grown on different soils except Torna were covered in the ranges specified by Mehta *et al.* (1969). But the Cu content of plant grown on Torna soil was very near the minimum value obtained by them. Therefore, it seems that in the case of this soil no response to Cu application is obtained. But this is the case of a soil which should be watched for Cu deficiency.

Minimum Cu uptake by wheat under control was 0.06 mg, per 4 kg. soil in Torna, while maximum was under Borsad soil 0.14 mg. per 4 kg. soil. It ranged between 0.06 and 0.28 mg./pot under soil application treatment and between 0.53 and 0.77 mg./pot under foliar spray. On hectare basis the minimum Cu removal by untreated wheat plants growing on Torna soil amounted to 34 g. and the maximum removal of 78 g. was observed in Borsad soil.

(*iv*) *Z*inc–maize crop :

Maize plants grown on the eleven soils under different treatments were healthy and symptoms of *Z*n deficiency were not observed on any of the plants. Overall statistical analysis of yield data revealed that neither the treatment effects nor their interaction effects were significant (Table 8).

TABLE 8

Effect of Zn application on the dry matter yield (in g.) of maize

(on oven-dry basis-mean of three replications)

Sr. No.	*Village*	*Control*	*Soil application*	*Foliar application*
1	Anand	9.2	9.3	8.9
2	Boriavi	12.1	12.0	13.5
3	Borsad	12.4	13.6	12.6
4	Gorwa	13.9	13.7	13.6
5	Limda	12.7	11.8	11.9
6	Mehmadabad	13.5	12.0	14.5
7	Sokhadakhurd	12.8	12.3	12.3
8	Tarapur	11.9	10.1	11.8
9	Thasra	14.4	13.6	15.0
10	Torna	9.3	10.4	11.6
11	Wankaner	12.0	10.2	11.1
	Mean	12.0	11.7	12.4

	L.S.D. @ 5%	S.Em.	C.V.%
Treatment	N.S.	0.25	11.7
Interaction	N.S.	0.81	11.5

Soil analysis has indicated that all the representative soils incorporated in the pot study contained sufficient amount of *Zn* except one from Torna, containing 0.54 ppm which was very near the marginal value of 0.5 ppm and is expected to be a *Zn*-responsive soil. Dry-matter yield of maize on this soil indicated some increase (though non-significant) in the yield over the control due to soil as well as foliar application of *Zn*.

Zinc content of plants grown under control treatment varied between 23.6 and 47.3 ppm (Table 9). Under soil application it ranged between 29.4 and 55.6 ppm and under foliar spray it varied from 76 to 205 ppm.

TABLE 9

Effect of different methods of Zn application on the Zn content and its uptake by maize

(mean of three replications)

Sr. No.	Village	Control		Soil application		Foliar application	
		Plant content (ppm)	*Uptake mg./pot*	*Plant content (ppm)*	*Uptake mg./pot*	*Plant content (ppm)*	*Uptake mg./pot*
1	Anand	23.6	0.22	42.4	0.39	109.6	0.98
2	Boriavi	30.8	0.37	42.4	0.51	93.2	1.26
3	Borsad	28.0	0.35	38.7	0.53	76.0	0.96
4	Gorwa	36.3	0.50	40.4	0.55	170.0	2.31
5	Limda	38.6	0.49	43.7	0.52	170.0	2.02
6	Mehmadabad	29.7	0.40	43.0	0.52	165.0	2.39
7	Sokhadakhurd	38.9	0.50	43.2	0.53	205.0	2.52
8	Tarapur	47.3	0.56	55.6	0.56	128.0	1.51
9	Thasra	26.2	0.38	29.4	0.40	160.0	2,40
10	Torna	36.3	0.34	51.2	0.53	150.0	1.74
11	Wankaner	37.0	0.44	48.4	0.49	187.5	2.08

Nair and Mehta (1958) reported 26.0 ppm of Zn in leaves of maize plants grown on *goradu* soil. Viets *et al.* (1953) reported that a Zn level of 15 ppm in the leaf of corn from the second node below the ear at silking was adequate for 100 to 125 bushel yields. The level at which response may occur varies with the variety, and even in the same crop variety, there may be difference depending on other nutritional or environmental factors. However, a generalization is made that plants with leaf Zn contents below 15 ppm are likely to respond to Zn treatment (Thorne, 1957). In the present study, the Zn content of plants grown in any of the soils was more than the values reported by Melsted *et al.* (1964), Benton Jones (1967) and Navrot and Ravikovitch (1968) for normal corn plants, indicating adequate Zn nutrition of maize plants.

Minimum uptake of Zn by maize plant grown in the control was 0.22 mg. per pot containing 3 kg. soil, while maximum observed was 0.56

mg. It ranged between 0.39 and 0.56 mg./pot under soil application treatment and between 0.96 and 2.52 mg./pot under foliar spray. When the uptake value was converted to hectare basis, minimum *Zn* removal by the above-ground portions of maize plants under control treatment amounted to 164 g. in Anand soil, while maximum amounted to 417 g. in Tarapur soil.

(v) Iron-sorghum crop :

None of the plants showed chlorotic appearance, which is a typical symptom of Fe deficiency. It has been mentioned under soil analysis that the quantity of available Fe of all the soils can be considered sufficient for normal plant requirement and may not respond to Fe application. Overall statistical analysis of yield data also indicated that neither the treatment effects nor their interaction effects were significant (Table 10). In general, on none of the soils beneficial effect of Fe application was observed indicating sufficiency of Fe in all the soils.

TABLE 10

Effect of Fe application on the dry matter yield (in g.) of sorghum

(on oven-dry basis-mean of three replications)

Sr. No.	*Village*	*Control*	*Soil application*	*Foliar application*
1	Anand	3.8	3.7	4.2
2	Boriavi	8.5	7.4	7.8
3	Borsad	13.0	12.5	10.7
4	Gorwa	13.2	12.8	15.1
5	Limda	11.0	11.5	13.3
6	Mehmadabad	11.8	12.0	10.8
7	Sokhadakhurd	9.4	7.6	7.1
8	Tarapur	11.5	11.4	13.5
9	Thasra	10.9	11.6	11.6
10	Torna	7.6	6.6	7.3
11	Wankaner	10.5	11.3	9.6
	Mean	10.1	9.9	10.1

	L.S.D. @ 5 %	S.Em.	C.V. %
Treatment	N.S.	0.17	11.1
Interaction	N.S.	0.60	11.6

Iron content of sorghum plants under control treatment varied from 338 to 562 ppm (Table 11). Similarly it ranged from 425 to 669 under soil application treatment and between 544 and 931 ppm under foliar

TABLE 11

Effect of different methods of Fe application on the Fe content and its uptake by sorghum

(mean of three replications)

		Control		*Soil application*		*Foliar application*	
Sr. No.	*Village*	*Plant content (ppm)*	*Uptake mg./pot*	*Plant content (ppm)*	*Uptake mg./pot*	*Plant content (ppm)*	*Uptake mg./pot*
1	Anand	469	1782	513	1898	856	3595
2	Boriavi	438	3723	628	4721	750	5850
3	Borsad	463	6019	562	7025	931	9962
4	Gorwa	562	7418	519	6643	744	11234
5	Limda	544	5984	562	6463	806	10720
6	Mehmadabad	488	5758	494	5928	700	7560
7	Sokhadakhurd	513	4822	669	5084	931	6610
8	Tarapur	513	5900	581	6623	906	12231
9	Thasra	413	4502	513	5951	906	10510
10	Torna	338	2569	438	2891	744	5431
11	Wankaner	531	5576	425	4803	544	5222

spray. The range obtained for Fe content of sorghum plants under control treatment is in accordance with that reported by Baser and Saxena (1970) for *jowar* plants grown on 14 different Rajasthan soils. The uptake value for Fe by sorghum plant under control showed a variation of 1.78 to 7.42 g. per pot containing 4 kg. soil. Under soil application treatment it varied from 1.90 to 7.03 g. per 4 kg. soil and from 3.60 to 12.23 g. per 4 kg. soil under foliar spray. Thus, the minimum uptake observed was 1 kg./ha (Anand soil), and the maximum was 4.15 kg./ha (Gorwa soil) when soils did not receive any Fe application either in the form foliar spray or as soil application.

(*vi*) **Molybdenum—alfalfa crop :**

All the plants appeared to be normal and deficiency symptoms of Mo were not found on the plants grown in pots on any of the soils. Average dry matter yield of all the four cuttings were pooled together to study the overall effect of treatments and are reported in Table 12.

TABLE 12

Effect of Mo application on the total dry matter yield (in g.) of four cuttings of alfalfa

(on oven-dry basis-mean of three replications)

Sr. No.	*Village*	*Control*	*Soil application*	*Foliar application*
1	Anand	7.8	7.2	6.3
2	Boriavi	14.8	15.3	14.5
3	Borsad	14.5	15.6	14.2
4	Gorwa	12.0	15.1	12.2
5	Limda	10.9	12.9	12.4
6	Mehmadabad	12.5	12.4	12.7
7	Sokhadakhurd	11.1	12.6	12.3
8	Tarapur	13.9	13.2	13.6
9	Thasra	12.6	13.0	12.7
10	Torna	8.5	9.8	8.0
11	Wankaner	11.3	13.2	12.7
	Mean	11.8	12.7	12.0

	L.S.D. @ 5 %	S.Em.	C.V. %
Treatment	0.6	0.21	10.1
Interaction	N.S.	0.68	9.6

Statistical analysis revealed that overall treatment effect was significant, but the interaction effect was not significant. Amongst the three treatments, application of Mo in the soil yielded significantly highest,

Under foliar spray the yields were intermediate but did not differ significantly from those of control. Though the interaction effect was not significant, foliar feeding of Mo of alfalfa raised on soils from villages Limda, Sokhadakhurd and Wankaner showed a tendency to increase the yield over that of control, while in Tarapur soil no such difference was observed. Torna soil, considered as Mo-deficient on the basis of soil analysis, showed an overall improvement in the yield of alfalfa when Mo was applied to the soil but no such beneficial effect was noted when fed foliarly. Thus, an overall positive response of Mo application was observed in increasing the yield of alfalfa.

Thus, in general, B, Mn and Fe application did not prove beneficial in increasing the yield of cauliflower., oats and sorghum respectively when grown in pots on some of the representative soils of Kaira and Baroda districts showing adequacy of these micronutrients in the soils studied. Molybdenum application proved beneficial in increasing the yield of alfalfa in some cases. Zinc fertilization gave a nonsignificant increase in the yield of hybrid maize on soil having its available zinc content just marginal. Copper application did not increase the yield of wheat on Torna soil but the plant content under control on this soil indicated that it was a case to be watched for Cu-deficiency in near future.

Summary

To study the response of applied micronutrients, pot experiments were conducted by taking Kaira and Baroda district soils having values of available micronutrients below the critical level for deficiency as indicated by soil analysis and also soil samples which gave values of available micronutrients somewhat higher than the critical level. The test crops selected were cauliflower for B, oats for Mn, wheat for Cu, maize for Zn, sorghum for Fe and alfalfa for Mo.

Soil analysis had indicated that B application on Anand soil may show positive response because of its low level in soils, but no such effect was actually observed in this experiment. Boron content of the plant was above 25 ppm giving evidence for adequate B nutrition. This shows that for soils having larger proportion of coarser fractions, somewhat lower available B can prove adequate.

Application of Mn did not improve the yield of oats on any of the soils and the Mn content of the plant was above 36 ppm in all cases. Similarly for sorghum crop there was no response to Fe application and the Fe content of plant was above 350 ppm. An increase in the yield of hybrid maize was obtained on Torna soil having marginal value of available *Zn* as indicated by soil analysis. On the same soil Cu application did not increase the yield, although soil analysis had indicated somewhat low Cu. Soils from Sokhadakhurd, Torna and Wankaner, which contained low available Mo, gave some response to Mo application.

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FLOWERING PLANTS OF THE GUJARAT UNIVERSITY CAMPUS AND ITS SURROUNDINGS (AHMEDABAD)

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Abstract

The paper describes flowering plants of the Gujarat University campus (excluding cultivated). General vegetation, climate and soils of the area are described and seasonal changes in vegetation are enumerated. Totally, two hundred seventy six species of flowering plants belonging to one hundred eighty genera and sixty four families (as per the classification of Bentham and Hooker) are recorded with their flowering periods and occurrence. Statistical analysis of the data is given.

Introduction

Flowering plants of Ahmedabad have been studied earlier by Saxton and Sedgwick (1918), Sutaria (1948, 1962), Gandhi (1958), Vaidya and Vora (1963), and Vaidya (1967). References of the occurrence of the flowering plants at Ahmedabad are also found in the work of Hooker (1897), Cooke (1901, 1958), Talbot (1902, 1949), Blatter and McCann (1935) and Shah (1963).

Gandhi (1958) reported 809 species of flowering plants (including cultivated species) from Ahmedabad and surroundings; however, species of the families, Cyperaceae and Gramineae have not been described. Vaidya (1967) has worked out flora of Ahmedabad excluding the cultivated plants. References of the occurrence of plants in the Gujarat University campus are found in the above work. However, they are incomplete. Hence, in the present work, plants of the Gujarat University campus and its surroundings are studied, with emphasis on the seasonal fluctuations.

The present work was done during 1962–63 and 1967–69. The plants collected from the area in various seasons were identified. Emergence, flowering period and occurrence were recorded. About one hundred and sixty herbarium sheets are lodged in the herbarium of the Botany Department of the Gujarat University and the rest are in the herbarium of L. M. College of Pharmacy, Ahmedabad. Name of the species, their families, habit, habitat, flowering period, occurrence and local name are set in Appendix I.

Study Site

Gujarat University campus is situated in the western part of Ahmedabad city beyond the river Sabarmati. Ahmedabad is situated at Lat. 23° 04' N, Long 72° 38′ E. The M.S.L. is 55 m.

The general topography of the area is almost plain with small ditches and depressions here and there. There are some abandoned paddy fields in the area. The site is now of extensive grasslands with scattered thorny bushes.

Climate

The climate of the area is tropical, monsoon dependent and semiarid. Winters (December to February) are mild with minimum temperature rarely reaching below 5°C. Summers (March to June) are hot and dry with absolute maximum temperature reaching 47.8°C. May is the hottest month. Rains are experienced only during monsoon months (end of June to October). Most of the rain is received during July, August and September (Table I). Average annual rainfall is 823 mm with total 37 rainy days. The rainfall is mostly scattered and erratic. According to Desai (1968), the mode of rainfall in Ahmedabad (including the University campus) varies : "(*i*) the commencement of the rains may be much earlier or considerably delayed than the normal date, (*ii*) there may be prolonged breaks in the rains, (*iii*) the rains may terminate earlier or persist longer than usual, and (*iv*) the rainfall may be unevenly distributed in space and time. "

Average annual humidity is 64% for morning and 37% for evening. Mean annual wind velocity is not high (6.9 km p.h.).

TABLE I

Climatic data for Ahmedabad

(From Climatological Tables, India Meteorological Department, Government of India)
Average of 30 years, 1931–1960.

Month	*Air Temperature in C (mean) Daily maximum*	*Daily minimum*	*Relative Humidity % morn-ing*	*Even-ing*	*Rainfall in mm*	*Number of rainy days*	*Mean wind velocity km p.h.*
January	28.7	11.9	55	28	3.9	0.4	5.4
February	31.0	14.5	52	24	0.3	0.1	5.1
March	35.7	18.6	47	20	0.9	0.2	7.3
April	39.7	23.0	49	18	1.9	0.2	7.8
May	40.7	26.3	68	21	4.5	0.3	9.5
June	38.0	27.4	77	41	100.0	4.2	10.8
July	32.2	25.7	86	68	316.3	13.2	10.8
August	31.8	24.6	84	69	213.3	11.1	8.3
September	33.1	24.2	80	60	162.8	5.6	7.0
October	35.6	21.2	64	35	13.1	1.0	4.6
November	33.0	16.1	52	29	5.4	0.6	4.1
December	29.6	12.6	56	29	0.7	0.1	2.6
Mean Annual	34.2	20.5	64	37	823.1	37.0	6.9

Soil

The soil of the area is old alluvium of the post-cretaceous age. It is coarse, sandy alluvium with calcium concretions lodged at a little depth. Soils show differences with slight change in physiography, being mostly sandy on elevations and clayey in depressions.

Vegetation

Most of the vegetation is xerophytic. *Capparis decidua* (Forsk.) Pax. *Dichrostachys cinerea* Wt. & Arn. and *Zizyphus nimularia* (Burn. f.) Wt. & Arn. are the most common scrubs.

In the grasslands, apart from the scrubs named above, the Leguminaceae plants like *Tephrosia purpurea* Pers., *Crotalaria medicaginea* Lam., and *Cassia tora* Linn. are common. In the sedges, *Cyperus rotundus* Linn. and in grasses *Dichanthium annulatum* (Forsk.) Stapf., *Cynodon dactylon* Pers., *Cenchrus ciliaris* Link., *Dactyloctenium aegypticum* (Linn.) Beauv., *Digitaria sanguinalis* Scop. are common.

Trees are rare. Small trees like *Streblus asper* Lour., *Acacia nilotica* Del. and *Salvadora persica* Linn. are found very sparsely situated.

Mangifera indica Linn. is a common cultivated tree. The common avenue trees in the area are : *Albizzia lebbek* Benth., *Azadiracta indica* A. Juss., *Cassia fistula* Linn., *Dalbergia sissoo* Roxb., *Gliricidia sepium* Stend., *Kigelia pinnata* DC., *Mimusops elingi* Linn., *Peltophorum inerme* Leaves, *Polyalthia longifolia* B. & H., *Restonea regia* Cooke and *Spathodea companulata* Beauv.

Medicinal Plants

A number of valuable medicinal plants grow wildly in the area. Among the important plants, mention may be made of the following :

Boerhaavia diffusa Linn.. *Cassia auriculata* Linn., *C. obtusa* Roxb., *Convolvulus pluricaulis* Choisy, *Citrullus colocynthis* Shrader, *Datura spp.*, *Eclipta prostrata* (Linn.) Linn., *Enicostemma littorale* Blume, *Sphaeranthus indicus* Linn., *Tinospora cordifolia* Miers, *Tribulus terrestris* Linn., and *Withania somnifera* Dun.

Seasonal Variations

The seasonal variation in the vegetation is directly related to the rainfall and subsequent period of hot and dry summer.

Immediately after the first rain, plants like *Cassia tora* Linn., *Crotalaria medicaginea* Lam., *Cyperus rotundus* Linn., *Cynodon dactylon* pers., *Tephrosia purpurea* Pers., come up in the open grounds. Other plants like *Achyranthes aspera* Linn., *Pupalia lappacea* Moq., *Peristrophe bicalyculata* Nees., *Xanthium strumarium* Linn., *Digitaria sanguidnalis* Scop., *Dichanthium annulatum* (Forsk.) Stapf. grow gregariously at later periods.

During the monsoon and post-monsoon periods, plants which colonize first as dominant species in the boggy situations are : *Ipomoea aquatica* Forsk., *Sagittaria sagittifolia* Linn., *Monochoria hasaetifolia* Presl,

and *Marsillea sp.* and various species of Cyperaceae. Others like *Ludwigia parviflora* Roxb., and *Ammania spp.* occupy the locality with drying of water in the post-monsoon period. At the end of November, when most of the water in boggy places begins to dry, the plants like *Hygrophila spinosa* T. Anders grow dominantly. When water is almost dried up from the soil surface, especially in the small ditches, plants like *Mollugo hirta* Thunb, *Vahlia viscosa* Roxb., *Sphaeranthus indica* Linn., *Coldenia procumbens* Linn., are commonly dominating. Most of the plants developing during post-monsoon period survive in winter. Majority of the annuals dry just before the onset of summer. In summer, only scrubby vegetation survives.

TABLE II

Number and percentage of families, genera and species of each class

	Dicotyledons Number	*Percentage*	*Monocotyledons* Number	*Percentage*	*Total*
Families	55	85.94	9	14.06	64
Genera	144	80.0	36	20.0	180
Species	213	77.18	63	22.82	276

TABLE III

Number and percentage of genera and species of the dominant families

Sr. No.	*Families*	*No. of Genera*	*Percentage*	*No. of Species*	*Percentage*
1.	Graminea	21	11.67	32	11.60
2.	Papilionaceae	15	8.33	26	9.42
3.	Cyperaceae	5	2.78	18	6.52
4.	Compositae	13	7.22	14	5.07
5.	Convolvulaceae	8	4.44	12	4.35
6.	Euphorbiaceae	6	3.33	12	4.35
7.	Amarantaceae	8	4.44	11	3.99

TABLE IV

Number and percentage of species belonging to the various habit

	Total Species	*Percentage*
1. Herbs	203	73.57
2. Shrubs	25	9.05
3. Climbers and Twiners	29	10.50
4. Trees	19	6.88
Total	276	100.00

TABLE V

Number and percentage of herbs

	Species	*Percentage*
(*a*) Aquatic herbs	13	6.42
(*b*) Prostrate herbs	55	27.09
(*c*) Erect herbs	135	66.49
Total Herbs	203	100.00

Statistical Synopsis

A total of 276 species of flowering plants are recorded, which belong to 180 genera of 64 families (Table II). The ratio of Monocotyledons to Dicotyledons is 1:6 of families, 1:4 of genera and 1:3 of species. The ratio of genera to species 1:1.5. The dominant families in the area are shown in Table III with percentage of their genera and species.

Out of a total 276 flowering species, 73.6 per cent are herbs, 9.0 per cent are shrubs, 10.5 per cent are climbers and twiners; however, trees are only 6.9 per cent (Table IV). Out of total 203 herbs occurring in the area, aquatic herbs are only 6.4 per cent, prostrate herbs are 27.1 per cent, while majority of herbs are with erect stem (66.5%) (Table V).

Parasitic plants are represented by three species, one of them is an epiphyte and climber (*Cuscuta reflexa* Roxb.). For details refer to Appendix I.

Observations and Discussion

Most of the species belong to Dicotyledons, however, family Gramineae is dominating in the area. The next important is the family Papilionaceae. Families like Cyperaceae and Compisitae also have more genera and species distributed in the area. Families, Convolvulaceae, Euphorbiaceae and Amarantaceae are also prominent in the area.

In general, herbs are dominating the area while trees, shrubs and climbers are very less. However, most of the herbs become dry as summer approaches. The scrubby species survive during the hot summers and continue to grow throughout the year. This indicates that the general vegetation is ephemeral and xerophytic.

Vaidya (1967) reported a total of 517 species of flowering plants from Ahmedabad and its surroundings. The Gujarat University campus is represented by 276 species of flowering plants, that is, 53.4 per cent of flowering plant species of Ahmedabad and its surroundings. Further, Vaidya has given the percentage of occurrence of species of the various families, as : Gramineae 11.32 %, Papilionaceae 8.36 %, Compositae 6.08 %, Convolvulaceae 5.13 %, Cyperaceae 5.32 %. These percentages coinside well with the present study (*cf.* Table III).

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APPENDIX I

Flowering Plants of the Gujarat University Campus

Sr. No.	Species	*Habit	**Flowering Period	***Occurrence	Local Name	Remarks
1	2	3	4	5	6	7
	Menispermaceae					
1.	*Cocculus hirsutus* (Linn.) Diels. Syn. *C. villosus* DC.	tw	10—12	1	Vevdi	
2.	*Tinospora cordifolia* Miers	C	3—5	1	Galo	
	Papaveraceae					
3.	*Argemone mexicana* Linn.	H.e.	1—2 10—12	1	Darudi	
	Cruciferae					
4.	*Brassica juncea* H. & T.	H.e.	1—12	1	Rai	Escaped
	Capparidaceae					
5.	*Capparis decidua* (Forsk.) Pax.	S	1—3 10—12	3	Kerada, Kaira, Karanda	
6.	*C. spinosa* Linn.	S	1—3	1	Govind	
7.	*Cadaba fruticosa* (Linn.) Druce Syn. *C. indica* Lam.	S	1—3 11—12	1	Khoradu	
8.	*Cleome viscosa* Linn.	H.e.	8—9	1	Pili talwan, Kanfuti	

1	2	3	4	5	6	7
9.	*C. monophylla* Linn	H.e.	10—11	R	—	
10.	*Gynandropsis gynandra* (Linn.) Briq. Syn. *G. pentaphylla* DC. Syn. *Cleome gynandra* (Linn.) Briq.	H.e.	6—7	1	Tanmani, Gandhari, Gandhatur	
Violaceae						
11.	*Hybanthus enneaspermus* (Linn.) Mueli. Syn. *Ionidium heterophyllum* Vent	H.e.	8—9	1	—	
Polygalaceae						
12.	*Polygala chinensis* Linn.	H.e.	8—10	1	—	
13.	*P. erioptera* DC.	H.e.	8—10	1	Bhoi-yasan	
Caryophyllaceae						
14.	*Polycarpaea corymbosa* Lam.	H.e.	10—11	2	Zinna pan-no okharad	
Portulacaceae						
15.	*Portulaca oleracea* Linn.	H.p.	9—12	1	Moti luni	
16.	*P. quadrifida* Linn.	H.p.	10—12	I	Zini luni	
Elatinaceae						
17.	*Bergia ammannioides* Roxb.	H.e.	10—12	1	Jal-Okharad	
18.	*B. odorata* Edgew	H.e.	10—12	2	Okharad, Gandharum	

Malvaceae					
19. *Abutilon indicum* SW.	S	8—12	2	Kanski, Khapat	
20. *Hibiscus cannabinus* Linn.	S	1—2	1	Ambhoi	
21. *Sida acuta* Burm.	S	7—12	2	Bala	
22. *S. cordifolia* Linn.	S	9—11	2	Mahabata, Khareti, Baladana	
23. *S. rhombifolia* var. *retusa* Masters.	H.e.	10—11	1	Shahdevi	
24. *S. spinosa* Linn.	H.e.	9—11	2	Kantalo bala	
25. *S. veronicifolia* Lam.	H.p.	8—11	1	Bhoybala	
Bombacaceae					
26. *Bombax ceiba* Linn. *pro parte* Syn. *Salmalia malabarica* (DC) Schott	T	1—3	R	Shimalo	Escaped ?
Sterculiaceae					
27. *Melochia corchorifolia* Linn.	H.e.	7—12	1	—	
Tiliaceae					
28. *Corchorus aestuanus* Linn. non Forsk. Syn. *C. acutangulus* Lam.	H.e.	8—9	1	Chha-dhari-chhunchh	
29. *C. capsularis* Linn.	H.e.	8—9	1	Moti-chhunch, Bor-chhunchh	
30. *C. fascicularis* Lam.	H.e.	8—9	1	Chhunchhadi, Ubhi-bahufali	
31. *C. olitorius* Linn.	H.e.	8—9	1	Moti-chhunchh	
32. *C. tridens* Linn.	H.e.	8—9	R	Chhunch	
33. *Triumfetta pilosa* Roth	H.e.	10—11	1	Zipati	
34. *T. rhomboidea* Jacq.	H.e.	9—12	1	Zipati	
35. *T. rotundifolia* Lam.	H.e.	8—12	1	Zipato	

1	2	3	4	5	6	7
Zygophylaceae						
36.	*Tribulus terrestris* Linn.	H.p.	8—11	3	Nannu Gokharu Betha-g.	
Simarubaceae						
37.	*Ailanthus excelsa* Roxb.	T	2—3	1	Araduso, Aralavo	
38.	*Balanites aegyptiaca* (Linn.) Delileo	t—S	2—5	2	Ingoriyo	
Meliaceae						
39.	*Azadiracta indica* A. Juss.	T	3—5	2	Limbado	Escaped.
Celastraceae						
40.	*Maytenus emarginata* (Wild). DH Syn. *Gymnosporea spinosa* (Forsk.) Fiori Syn. *G. montana* Benth	S	10—11	R	Vikaro	
Rhamnaceae						
41.	*Zizyphus mauratiana* Lam. Syn. *Z. jujuba* Lam. non Mill	t	9—11	R	Bor	
42.	*Z. nimularia* (Burn. f.) Wt. & Arn.	S	9—11	2	Chanibor	
Ampelidaceae						
43.	*Caryratia carnosa* Gagnep. Syn. *Cissus carnosa* Lam.	C	7—8	2	Khat-khatumbo	
44.	*C. latifolia* vanl	C	7—9	1	Jangli-draksha	
Sapindaceae						
45.	*Cardiospermum halicacabum* Linn.	C	8—11	1	Kagdolio	

Papilionaceae

45. *Cardiospermum halicacabum* Linn.	C	8—11	1	Kagdolio	
Papilionaceae					
46. *Abrus precatorius* Linn.	C	9—10	1	Chanothi, Gunji	
47. *Aeschynomene indica* Linn.	H.e.	9—11	2	Bhmoy-ikad	
48. *Alhagi camelorum* Fisch.	H.e.	2—3	R	Javaso	
49. *Alysicarpus rugosus* DC.	H.e.	9—11	1	Samervo	
50. *A. vaginalis* (Linn.) DC.	H.p.	8—11	2	Bhoi-samervo	
51. *Butea monosperma* (Lam.) Taub.	t	2—3	R	Khakharo, Kesudo	Near Pratima Society
52. *Canavalia gladiata* Jacq. Syn. *C. ensiformis* DC.	tw	8—10	1	Abbo, Talvardi	
53. *Clitoria ternatea* Linn.	tw	8—10	2	Garani, Bibri, Koyal	
54. *Crotalaria burbia* Ham.	S	1—2	1	Kharasan	
55. *C. medicaginea* Lam.	H—e	7—11	3	Rammethi	
56. *C. mysorensis* Roth.	H—e	10—11	1	—	Vaidya, (1967)
57. *C. retusa* Linn.	H—e	7—9	1	Ghugharh	
58. *Desmodium triflorum* (Linn.) DC.	H—p	9—10	1	Zinako-pandadio	
59. *Flemingia lineata* Roxb	S	1—2	1	—	
60. *Indigofera cordifolia* Heyne ex Roth.	H—p	8—11	1	Bavachi, Dalio	
61. *I. echinata* Willd.	H—p	8—10	1	—	
62. *I. enneaphylla* Linn.	H—p	7—12	3	Bhmogali	
63. *I. hirsuta* Linn.	H—e	8—10	1	Runchhaligali	
64. *I. trifoliata* Linn.	H—e	8—10	1	Rati-methi	
65. *Mucuna prurita* Hook	tw	8—12	1	Kounch, Kavach, Kuvech	

1	2	3	4	5	6	7
66.	*Rhynchosia bracteata* Benth. ex Baker	tw	8—10	1	Nani-kamarvel	Vaidya & Vora (1964)
67.	*R. minima* (Linn.) DC.	tw	8—10	1	Nani-kamalvel	
68.	*Sesbania bispinosa* (Jacq.) F. & R.	S	8—9	R	—	
69.	*S. procumbens* W. & A.	S	—	1	—	Vaidya & Vora (1964)
70.	*Tephrosia purpurea* (Linn.) Pers.	H—e	8—12	4	Sarapankho, Ghodakan	
71.	*T. villosa* Pers.	H—e	8—12	1	Ranchhalo-sarapankho	
Caesalpinaceae						
72.	*Cassia auriculata* Linn.	S	1—12	2	Aaval	
73.	*C. obovata* Roxb	H—e	8—11	1	Mindhi-Aaval	
74.	*C. occidentalis* Linn.	H—e	9—11	1	Kasundro	
75.	*C. pumila* Lamk	H—p	8—10	2	Chamediyum	
76.	*C. tora* Linn.	H—e	8—11	2	Kunvadiyo	cultivated but escaped
77.	*Parkinsonia aculeata* Linn.	t	1—	1	Ram-baval	
78.	*Tamarindus indica* Linn.	T	5—7	1	Aambali	cultivated but escaped
Mimoseae						
79.	*Acacia nilotica* Del. Syn. *A. arabica*	T	7—12	3	Baval	
80.	*Dichrostachys cinerea* (Linn.) Wt. & Arn.	S	8—10	2	Marudh, mor dhundhiyun	
81.	*Mimosa hamata* Willd	S	9—10	1 R	[illegible]	

Wt. & Arn.

81. *Mimosa hamata* Willd	S	9—10	1—R	Kasi	
82. *Pithecolobium dulce* Benth	t	1—3	1	Goras-aambali	
83. *Prosopis spicigera* Linn.	T	1—3	1	Khijado, Sami	
Saxifragaceae					
84. *Vahlia dichotoma* (Murr.) Kze. Syn. *V. viscosa* Roxb.	H—p	11—12	2	Pilo-aagiyo	
Lythraceae					
85. *Ammania baccifera* Linn.	H—e	11—12	1	Jal-aagiyo	
86. *A. multiflora* Roxb	H—e	11—12	1	—	
Onagraceae					
87. *Jussiaea peremnis* (Linn.) Brenan. Syn. *Ludwigia parviflora* Roxb.	H—e	2—3	1	Lavingia	
88. *Trapa bispinosa* Roxb	H—aq.	7—8	1	Shingoda	Probably introduced
Cucurbitaceae					
89. *Blastania garcini* Cogni.	C	7—9	1	Aankh-futamani	
90. *Citrullus colocynthis* Scharader	C	7—9	1	Indravarna, Indrana	
91. *Coccinia cordifolia* (Linn.) Cogn. Syn. *C. indica* Wt. & Arn.	C	7—9	1	Kadavi-gholi.	
92. *Melothria maderaspatana* Cogn.	C	7—9	1	Chanak-chibhadi	
93. *Momordica charantia* Linn.	C	7—9	1	Kareli	
94. *M. dioica* Roxb.	C	7—9	1	Kantola, Kankoda	
95. *Trichosanthes cucumerina* Linn.	C	7—9	1	Kadvi-padar, Padvel, Kadva patola, Ran paryar	

1	2	3	4	5	6	7
Ficoideae						
96.	*Gisekia pharnaceoides* Linn.	H—p	8—9	1	—	
97.	*Trianthema decandra* Linn. Syn. *T. pentandra* Linn.	H—p	8—11	1	—	
98.	*T. portulacastrum* Linn. Syn. *T. monogyna* Linn.	H—p	7—9	3	Satodo	
Molluginaceae						
99.	*Glinus lotoides* Linn. Syn. *mollugo hirta* Thumb.	H—p	1—4	3	Mitho-Okharad	
100.	*G. oppositifolia* (Linn.) A. DC.	H—p	9—10	1	Kavado-Okharad	
101.	*Mollugo pentaphylla* Linn.	H—p	8—9	1	Zaras	
Rubiaceae						
102.	*Borreria hispida* (Linn.) F.N. Will. Syn. *Spermacoce hispida* Linn.	H—p	7—10	2	Kharsat, Shankhal Madhuri-jadi	
103.	*B. stricta* (Linn. f.) Sch.	H—e	7—9	2	Gandhio	
104.	*Oldenlandia corymbosa* Linn.	H—e	8—10	2	Parpat, Pit-papad.	
105.	*O. umbellata* Linn.	H—e	8—10	1	—	
Compositae						
106.	*Acanthospermum hispidum* DC.	H—e	1—2 1—3	1	Safed-sedardi, Mankad-mari,	
107.	*Ageratum conyzoides* Linn.	H—e	11—12	2	Ajagandha, Gandhari	

107. *Ageratum conyzoides* Linn.	H—e	11—12	2	Ajagandha, Gandhari
108. *Blumea lacera* (Burm. f.) DC.	H—e	1—3	2	Kapurio, Kalhar, Kok-ronda
109. *Caesulia axillaris* Roxb.	H—e	8—12	3	—
110. *Echinops echinatus* Roxb.	H—p	9—12	2	Shulio, Utkanth
111. *Eclipta prostrata* (Linn.) Linn.	H—p	10—12	2	Bhangaro
112. *Launaea nudicaulis* Hook	H—p	9—12	2	Bhoipatri
113. *Sonchus oleraceus* Linn.	H—e	9—12	2	Dudhari-sonki
114. *Sphaeranthus indicus* Linn.	H—p	10—12	3	Gorakh-mundi, Bodiyo kalhar
115. *Tricholepis radicans* DC.	H—p	9—12	1	Benthu-fusiarun
116. *Tridex procumbens* Linn.	H—p	7—12 1—3	3	Paradeshi-bhangaro
117. *Vernonia anthelmintica* Wild.	H—e	12, 1—2	1′	Kadavi-jiri
118. *V. cinerea* (Linn.) Less.	H—e	1—2	2	Sadedi, Savedi, Sadevi
119. *Xanthium strumarium* Linn.	H—e	1—3 11—12	3	Gadarium
Plumbaginaceae				
120. *Plumbago zeylanica* Linn.	H—e	8—9	1	Chitro, Chitrak
Sapotaceae				
121. *Manilkara hexandra* (Roxb.) Dub. Syn. *Mimusopa hexandra* Roxb	t	9—11	1	Rayan
Salvadoraceae				
122. *Salvadora oleoides* Decaisne	t	1—3	1	Mithijar, Pilu, Khakhar
123. *S. persica* Linn.	t	1—2 11—12	1	Kharijav, Piludi

1	2	3	4	5	6	7
Apocynaceae						
124.	*Lochnera pusilla* Sch.	H—e	7—9	2	Karapati-rai, Parvati-rai	
Asclepiadaceae						
125,	*Calotropis gigantea* (Linn.) R.Br.	S	1—8	1	Rato-aankado, Moto-aankhado	
126.	*C. procera* (Ait) R.Br.	S	1—3 8—12	2	Aankhado, Noano-aankado	
127.	*Leptadenia reticulata* Wt. & Arn.	tw	6—9	2	Nani-dodi	
128.	*Marsdenia Volubilis* (Linn. f.) T. Cooke	tw	1—3	1	Moti-dodi	
129.	*Pergularia daemia* B. & M.	tw	8—12	1	Chamar-dudheli	
130.	*Telosma pallida* (Roxb.) Craib. Syn. *P. pallida* Wt. & Arn.	tw	9—12	1	Vasatavari, Kadina ful	
Gentianaceae						
131.	*Enicostemma verticillatum* (Linn.) Engl. Syn. *E. littorale* Blume	H—e or p.	8—12	2	Mamejavo, Kadavi-nani	
Hydrophyllaceae						
132.	*Hydrolea zeylanica* Vahl	H—aq	9—12	1	Popati (?)	
Boraginaceae						
133.	*Coldenia procumbens* Linn.	H—p	9—12	3	Basario-okharad	
134.	*Ehretia laevis* Roxb.	t	1—5	R	Vedhivaro	
135.	*Helitropium indicum* Linn.	H—e	9—12	2	Hathi-sundha	

134. *Ehretia laevis* Roxb.	t	1—5	R	Vedhivaro	
135. *Helitropium indicum* Linn.	H—e or p	9—12	2	Hathi-sundha	
136. *H. marifolium* Ratz.	H—p	1—2	1	Zinaku hathi-sundh	
137. *H. supinum Hochst.* Syn. *H. zeylanicum* Linn.	H—c	10—12	1	Hathi-sundh	
Convolvulaceae					
138. *Argyreia nervosa* Boj.	tw	8—10	1	Varadharo	
139. *Convolvulus arvensis* Linn.	H—p	1—3, 12	3	Veladi, Khetarau-fudaradi, Haran padi.	
140. *C. plurpcaulis* Choisy.	H—p	11—12	2	Shankh-puspi, Shankhavali	
141. *Cressa cretica* Linn.	H—p	11—12	1	Padio, Palio	
142. *Cuscuta reflexa* Roxb.	tw	1—2	1	Amar-vel	
143. *Evolvulus alsinoides* Linn.	H—p	7—12 1—3.	2	Kali-shankhavali, Zinki-fudaradi	
144. *Ipomoea aquatica* Forsk.	H—aq	10—12	2	Jal-gamini, Nad-ni-vel	
145. *I. biloba* Forsk.	H—p	8—12	1	Aarvel	
146. *I. palmata* Forsk.	tw	1—12	1	Naravel	Escaped.
147. *I. pes-tigridis* Linn.	tw	8—11	1	Vagh-padi	
148. *Merremia gengetica* (Linn.) Cuf. Syn. *M. emarginata* Hal. f.	H—p	9—11	3	Undarkani	
149. *Rivea hypocrateriformic* Choisy	C	8—10	1	Phang	
Solanaceae					
150. *Datura innoxima* Mill	S	9—12	1	Kalo-daturo	
151. *D. metel* Linn.	S	9—12	1	Dholo-daturo	

1	2	3	4	5	6	7
152.	*Physalis minima* Linn.	H—e	8—11	2	Popati, Parapoti	
153.	*Solanum indicum* Linn.	S	8—10	1	Vad-ringani-Dorali	
154.	*S. nigrum* Linn.	H—e	9—12	1	Kanparu, Piludi	
155.	*S. surattense* Burn. f. Syn. *S. zanthocarpum* S. & W.	H—p	1—5 10—12	2	Bhoin-ringani	
156.	*Withani somnifera* Dunal	H—e	9—12	2	Ghodakun, Aswagandha	
Scrophulariaceae						
157.	*Bacopa moniera* (Linn.) Pennell	H—p	1—4	2	Kadavi-luni, Jalnevri Bam.	
158.	*B. brachiata* L. & O.	H—e	8—9	1	—	
159.	*Bonnaya oppositifolia* Spreng	H—e	8—9	1	—	
160.	*Linnophila indica* Druce	H—aq	11—12	1	Turati	
161.	*Lindenbergia indica* (Linn.) O. Kuntze	H—p	9—12	1	Bhint-chatti, Patthar-chatti.	
162.	*Striga euphrasioides* Benth.	H—e	8—11	2	Dhoro-aagio	
163.	*S. gesneroides* (Wild.) Watke. Syn. *S. orobanchioides* Benth	H—e	9—11	2	Rato-aagio	
164.	*Verbascum chinense* Sant. Syn. *V. coromandelianum* (Vahl.) O. Kunte.	H—e	1—4	1	Kalhar	
Lenibulariaceae						
165.	*Utricularia stellaris* Linn.	H—aq	9—12	1	Arkzaver	

165. *Utricularia stellaris* Linn.	H—aq	9—12	1	Arkzaver	
Pedaliaceae					
166. *Pedalium murex* Linn.	H—e	9—12	1	Mota-Gokhuru, Kadava **g.** Ubha g.	
Martyniaceae					
167. *Martynia annua* Linn.	H—e	8—12	1	Vinchudo	
Acanthaceae					
168. *Hygrophila auriculata* (Sch.) Heine	H—e	7—12	2	Akharo	
169. *H. polysperma* T. Anders.	H—e	7—12	2	—	
170. *Justicia diffusa* Willd.	H—p	8—12	2	Akharo	
171. *J. simplex* D. Don.	H—p	8—11	1	—	
172. *Paristrophe bicalyculata* (Retz.) Nees.	H—e	9—11	2	Kali-andhedi, lasi-a.	
173. *Rostellularia procumbens* (Linn.) Nees.	H—e	9—11	1	—	
Verbenaceae					
174. *Clerodendron phlomidis* Linn. f.	S	1—2 8—12	1	Arani, Tankaro	
175. *Phyla nodiflora* Michxo	H—e	7—12	2	Rat-velio, Ratulio	
Labiatae					
176. *Leonotis nepetifolia* Br.	H—e	8—9	1	Mati-shal	
177. *Leucas aspera* Spreng.	H—e	10—12	1	Kubo	
178. *L. cephalotes* Spreng.	H—e	11—12	1	Doshino-kubo, Khetarau **kubo**	
179. *Ocimum americanum* Linn.	H—e	8—12	1	Aajolo	
180. *O. basilicum* Linn.	H—e	7—11	1	Damaro, Sabajo	Escaped ?
181. *O. gratissimum* Linn.	H—e	7—12	1	Aavachi.bavachi	

1	2	3	4	5	6	7
	Nyctaginaceae					
182.	*Boerhaavia diffusa* Linn.	H—p	8—12	3	Satodi, Punarnava Vakhakhakharo	
183.	*B. rependa* Willd.	H—p	9—12	1	Satodo, Punarnava	
184.	*B. verticillata* poir.	H—e—p	8—12	1	Moto-satido, Moto-satodo	
	Amarantaceae					
185.	*Achyranthus aspera* Linn.	H—e	9—12	3	Andhadi, Zipato	
186.	*Aerua javanica* (Burm. f.) Juss	H—e	8—11	1	Buvado	
187.	*A. lanata* Juss.	H-e or p	8—11	2	Gorakh-ganjo, Bhoin-jadi	
188.	*Alternanthera sessilis* R. Br.	H—p	7—12	2	Panibhaji, Jaljambavo	
189.	*Amarantus spinosus* Linn.	H—e	8—12	2	Kantaro-dabho, Dhimaro	
190.	*A. tenuifolius* Willd	H—e	8—12	1	—	
191.	*A. viridis* Linn.	H—e	8—11	1	Nano-tadalajo	
192.	*Celosia argentea* Linn.	H—e	9—12	1	Lambadi, Lampadi	
193.	*Digera alternifolia* (Linn.) Archers. Syn. *D. muricata* Mart.	H—e	8—12	2	Kanejaro, Kanjo	
194.	*Gomphrena celosioides* Mart.	H—p	7—12	2	—	
195.	*Pupalia lappacea* Moq.	H—e	8—12	2	Dhoro-zipato	
	Chenopodiaceae					
196.	*Chenopodium album* Linn.	H—e	1—3	1	Chilani-bhaji	

Euphorbiaceae					
197. *Acalypha ciliata* Forsk.	H—e	8—10	1	Venchi-kanto	
198. *A. indica* Linn.	H—e	8—10	2	Khokali, Dadaro, Venchikanto	
199. *Chrozophora tinctoria* A. Juss.	H—p	11—12	2	Kalo-okharad, Okharad	
200. *Euphorbia hirta* Linn.	H—p	1—12	3	Nagala-dudheli, Rati-duo	
201. *E. hypericifolia* Linn. Var. *parviflora Hook*.	H—p	8—12	2	Dudhi, Kakar-dhumaro	
202. *E. microphylla* Heyne.	H—p	1—12	2	Dudhi, Ek-fuli-dudhi	
203. *E. nertifolia* Linn.	S	2—4	2	Thor, Bhungalo-thor	Planted for hedge
204. *E. thymifolia* Linn.	H—p	1—12	2	Nani-dudheli, Zinki-dudheli	
205. *E. tirucalli* Linn,	S	8—10	1	Kharasani, Kharasadi-thor	Common in hedges
206. *Jatropha curcas* Linn.	S	9—11	1	Ratanjot, Mogalai-arendo	
207. *Phyllanthus fraternus* Webster	H-e or p	7—9	2	Bhoin-aambali	
208. *Securinega leucopyrus* (Willd) Mu-ell-Arg. Syn. *Fluggea leucophrus* Willd	S	4—5	1	Shivano.	
Moraceae					
209. *Ficus religiosa* Linn.	T	4—6	1	Pipalo, Peepal	Cultivated and escaped
210. *F. tsiela* Roxb.	t	4—9	1	Pipali	”
211. *Streblus asper* Lour.	t	1—3	1	Kharoti, Saroti, Sarori	
Ulmaceae					
212. *Holoptelea integrifolia.*	T	2—3	1	Charel, Kanzo, Popati	

1	2	3	4	5	6	7
	Ceratophyllaceae					
213.	*Ceratophyllum demersum* Linn.	H—aq	8	1	—	
	Lillaceae					
214.	*Asphodelus tenuifolius* Car.	H—e	10—12	2	Dungaro	
215.	*Gloriosa* Superba Linn.	C (H)	7—10	1	Kankasani	
	Pontederiaceae					
216.	*Monochoria hastaefolia* Presl.	H—aq	11—12	1	—	
217.	*M. vaginalis* Prest.	H—aq	11—12	1	—	
	Commelinaceae					
218.	*Commelina benghalensis* Linn.	H—p	8—12	2	Motu-shish-muliyum	
219.	*C. diffusa* Brum. Syn. *C. nudiflora* Linn.	H—p	10—12	1	Shish-muliyum	
	Lemnaceae					
220.	*Lemna gibba* Linn.	H—aq	8—9	1	—	
221.	*L. polyrhica* Linn.	H—aq		2 1—R	—	Vaidya & Vora (1964)
222.	*Wolffia michelli* Schleid.	H—aq	8—9	1	—	”
	Alismaceae					
223.	*Butomopsis lanceolata* Kunth	H—e	11	1	—	
224.	*Sagittaria sagittifolia* Linn.	H—aq	8—9	1	—	

Naiadaceae				
225. *Aponogeton monostachyon* Linn.	H—aq	7—12	1	—
Eriocaulaceae				
226. *Eriocaulon trilobum* Buch-Ham.	H—e	9—10	1	—
Cyperaceae				
227. *Bulbostylis barbata* Kunth.	H—e	8—9	1	—
228. *Cyperus articulatus* Linn.	H—e	9—10	1	—
229. *C. arvenarius* Retz.	H—e	10—11	1	
230. *C. bulbosus* Vahl.	H—e	10—11	1	Thek
231. *C. compressus* Linn.	H—e	10—11	1	—
232. *C. difformis* Linn.	H—e	10—12	1	—
233, *C. iria* Linn.	H—e	10—11	1	—
234. *C. kyllingia* Endl. Syn. *kyllinga monocephala* Rottb.	H—e	9—10	1	—
235. *C. niveus* Retz.	H—e	10—11	1	—
236. *C. rotundus* Linn.	H—e	8—11	3	Moth, Chida-moth, Montha
237. *C. triceps* (Rottb.) Endl. Syn. *kyllinga triceps* Rottb.	H—e	8—10	1	—
238. *Fimbristylis bisumbellata* (Forsk.) Bub.	H—e	9—11	1	—
239. *F. littoralis* Gaud.	H—e	9—10	1	—
240. *Remirea maritima* Aubl.	H—e	10—12	1	—
241. *Scipus articulatus* Linn.	H—e	9—10	1	—
242. *S. kysoor* Roxb.	H—e	9—11	1	—

1	2	3	4	5	6	7
243.	*S. litoralis* schard.	H—e	10—12	1	—	
244.	*S. roylei* (nees) Beetle.	H—e	10—12	1	—	
	Gramineae					
245.	*Andropogon contortus* Linn.	H—e	11—12	2	Zinzavo	
246.	*A. iwarancus* Jones.	H—e	11—12	R	—	
247.	*Apluda varia* Hack.	H—e	10—11	1—R	—	
248.	*A. mutica* Linn.	H—e	10—12	R	—	
249.	*Aristeda depressa* Retz.	H—p	10—12 1—3	2	—	
250.	*Arundinella nepalensis* Trin.	H—e	10	1	—	
251.	*Cenchrus Ciliaris* Link.	H—e	10—11	3	Anjan ghas	
252.	*C. setigerus* Vahl. Syn. *C. biflorus* Roxb.	H—e	10—11	1	Dhraman ghas	
253.	*Chloris barbata* Sw.	H—e	10—12	1	—	
254.	*C. dolichostachya* Lagasca	H—e	10—12	1	—	
255.	*C. virgata* Sw.	H—e	1—2	1	—	
256.	*Cynodon dactylon* (Linn.) Pers.	H—p	1—12	3	Dhro, Dharo	
257.	*Dactyloctenium aegypticum* (Linn.) Beauv.	H—p	10—12	2	Vad-chaman, Choto	
258.	*D. sindicum* Boiss.	H—p	8—12	2	Chaman	
259.	*Dichanthium annulatum* (Forsk) Stapf.	H—e	9—11	1	—	

260. *Digitaria sanguinalis* Scop.	H-p or C	9—11	2	—
261. *Eragrostis ciliaris* Link. Var. *brachystachya* Boiss.	H—e	10—11	2	Marmar
262. *E. diarrhena* (Schult) Stend.	H—e	10—12	2	—
263. *E. stenophylla* Hochst. ex Miq.	H-e (or P)	10—11	1	—
264. *E tenella* Roem & Schult Var. *plumosa Stapf.*	H—e	10—11	1	Bar-bhuri, Barbusi
264-a. *E. t.* Var viscosa Stapf.	H—e	10—11	1	Chikti
265. *Heteropogon contortus* (Linn.) Beauv.	H—e	9—10	1	Nani-sunkhali
266. *Imperata arundinacea* Cyrill.	H—e	9—10?	1	—
267. *Ischaemum rugosum* Salisb.	H—e	10—11	1	—
268. *Iseilema prostratum* (Linn.) Anders	H—e	11	2	—
269. *Melanocenchrus jacquemontii* Jauv. & Spach.	H—e	10—11	1	—
270. *Panicum javanicum* Poir.	H—e	8—11	1	—
271. *P. psilopodium* Trin.	H—e	9	1	—
272. *Pennisetum dichofomus* Delile	H—e	11—12	1	—
273. *Saccharum Spontaneum* Linn.	H—e	11	1—R	—
274. *Setaria glauca* (Linn.) Beauv.	H—e	8—11	1	Zipati-ghas, Kunchi
275. *S. rhachitricha* T. Cooke	H—e	10—11	1	Kutara-ghas
276. *Sporobolus diander* Beauv.	H—e	10	2	—

* Habit

H—aq = Aquatic Herb
H—e = Herb erect
Hp = Herb prostrate or creeping on on ground
C = Climber
S = Shrub
t = Small tree
tw = Twinner
T = Big tree

** Flowering period

1. January
2. February
3. March
4. April
5. May
6. June
7. July
8. August
9. September
10. October
11. November
12. December.

*** Occurrence

R = Ratre
1 = Occassional
2 = Common
3 = Most common
4 = Abundent

FACTORS RESPONSIBLE FOR THE SLOW PROGRESS IN INCREASING PRODUCTIVITY OF OILSEED CROPS

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No adequate attention has been paid to the improvement of oilseed crops in our country due to their subsidiary importance in our daily life. More attention was concentrated on staple crops—cereal crops—where it has been possible to make a significant headway in improvement of wheat, maize, rice, bajra and jowar. Now the work is being intensified on pulses. The oilseed crops occupy only 11.2 % i.e, 15.5 million hectares of total area under cultivation in this country, and oilseed crops being; castor, coconut, groundnut, linseed, niger, rape seed, mustard, safflower and sesame (19), major ones being; groundnut (*Arachis hypogaea* L.), sesame (*Sesamum indicum* L.), rape seed, mustard (*Brassica* sp.), linseed (*Linum Usitatissimum* L.) and castor (*Ricinus communis* L.) (18), and the last one being non-edible. I shall be discussing different aspects associated with the slow progress of groundnut, sesame, linseed and rape and mustard only.

Groundnut and sesame (kharif crops) are rainfed crops and are dependent on rains. Toria is an irrigated crop in Punjab and submontane regions but brown sarson is rainfed or receive irrigation alongwith rabi cereals or gram in mixed cropping. Sometimes groundnut and sesame are raised as rabi crops also in some area, but too less when compared with kharif crop (18). Thus it may be concluded that oilseed crops in our country mainly depend upon rainfall.

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Factors associated with poor yields of oilseed crops :

1. **Environmental factors :** The oil content is influenced by environmental factors especially weather conditions during maturation phase, the amounts of nutrients available and stage of maturity at harvest. The variations between years in oil content are mainly caused by climatic factors. If there is sufficient water in the soil, high temperatures during ripening favour a high oil content. Nitrogen is of great importance in influencing oil content but it has been shown conclusively that very high applications of nitrogen cause a decrease in oil content. Oil is generally formed to a large extent towards the end of ripening period, and the oil content is also influenced by the ripening stage at harvest, early harvest resulting in lower oil content. Despite the influence of environment the oil content is very much less variable than the seed yield. The variation between individual plants in regard to oil content depends to a considerable extent upon genetic differences, while in regard to seed yield these are completely overshadowed by environmental conditions (26).

Yield fluctuations are available from year to year in the same area and from region to region in the same year in case of groundnut. Distribution and amount of rainfall directly effect groundnut production. Early maturing bunch types are less adversely effected than late maturing spreading types, if there is good rainfall during early stages and insufficient during late growth and developmental stages of groundnut. Black soils with higher moisture retentive capacity and low rainfall contribute to higher yields in comparison to lighter or well drained soils. Excessive rains also lower yields in such heavy soils. Sesame suffers heavily from water logging even for shorter periods. Humid and cloudy weather increases depredation by pests and diseases in mustard and linseed (18). Thus weather conditions play a vital role in production of oil seeds crops in our country and especially in case of groundnut where we should study the interaction of rainfall and soil types thoroughly.

2. **Physiological factors :** Plant physiology has been a neglected subject for a long time in our country and still its due importance is not being recognised. It is clear from the fact that in most of our Universities, colleges and research Institutes, there are no adequate facilities, well equipped laboratories and trained research personnel to do basic and

applied research in plant physiology (10). Thus it is true that the major oilseed crops of India have not so far been subjected to basic physiological investigations (18), and in this way the plant physiologists could not contribute their share and help plant breeders in selecting varieties suitable to meet our demands. Of course, now, a start has been made by the plant physiologists, in spite of the above mentioned difficulties, information now is avaliable, although of preliminary nature, for selecting drought resistant varieties, and physiologically better varieties.

In case of bunch varieties of groundnut which are non-dormant, they would sprout in the field, if there are continuous rains at the time of harvest (20). This aspect has been confirmed with Spanish Improved variety and a loss of Rs. 89/- per hectare was estimated owing to reduction in the quality alone; loss in yields of pods was not worked out (21). Water-soluble auxin-like substances in the seeds appear to be responsible for the non-dormant nature of the bunch varieties (25). It might be possible to suppress the synthesis of these auxin-like substances by foliar application of maleic hydrazide, which antagonizes auxins (22) and induces dormancy. Maleic hydrazide (500 ppm) reduced the sprouts better in pot trial in TMV–2 and Spanish Improved and in field trial 200 ppm gave significantly lesser sprouts and pod-yield was not affected when the chemical was sprayed at kernel-development stage (21). Similarly coumarin (1500 ppm) induces dormancy in non-dormant groundnut seeds of TMV–2 and lowered amount of ascorbic acid (32). CCC (Cycocel) 2000 ppm likewise inhibits germination of groundnut var. AH 334 during the juvenile phase (9). Thus the chemical use of these substances will open new avenues in researches on increasing yields of groundnut.

There is a positive correlation between root volume and drought resistance in case of groundnut. The drought resistant variety senegal 47–16 had maximum nitrogen 4.38 % at the time of floral initiation. Short internodes were associated with drought resistance. Gujarat groundnut drought resistant variety 'Narrow leaf' has thick cuticle layer on leaves and less number of stomata per unit area than other varieties (18). Use of antitranspirants will be of great help in checking rate of transpirational lossess of water to a large extent. 36 varieties of potatoes were screened for internodal patterns and it was pointed that 23 early varieties had larger

proportions of internodes with long retarded phase while remaining 13 late varieties had larger proportions of long accelerated phase (23).

In drought resistant variety of sesame N.P. 6, water absorption rate is attained 4 hours after peak day temperature and there was higher oil content than other varieties which attained peak water absorption rate 5 hours after peak day temperature and had less oil content. In addition to this the resistant variety had broad and lobed leaves which later on became narrow and lanceolate, thus reducing leaf area transpiration in later stages of growth (18). Moisture stress reduced carbohydrates more in leaves than any plant part in tomato. On rewatering of water-stressed plants a very rapid and marked increase of starch with a corresponding increase in reducing and non-reducing sugars was evidenced (30).

Essential changes in hardening of plants seems to be an increase in the ability of proteins to absorb water (hydrophily). One of the best ways to increase heat tolerance is to harden plants at low temperature. Low temperature reduces the growth rate and salts and sugars accumulate in the cells. The results is, an increase in osmotic pressure of cell vacuoles and withdrawal of water from the protoplasm. This in turn increases hydrophily in plants (13). Indoleacetic acid or 2, 4–D when applied to the pea stem sections greatly reduced the amount of protein coagulated by heat from extracts of these tissues. Total protein content was not altered, only the coagulation threshold. Gibberellic acid, which also promotes stem growth enhanced the auxin effect on proteins. Thus growth substances, like IAA, 2, 4–D, GA and AA probably play a part in heat hardening (8, 14, 15).

Pre-sowing hardening method for dry farming conditions in our country has been advocated due to the superiority of pretreated seeds in having higher dry matter production, relative growth rate of seeds and seedlings not only under full water conditions but also under restricted watering as well as under drought and salinity conditions. The pretreated seeds extract moisture from the atmosphere more efficiently because of the fact that alternate drying and soaking makes the seed more hydrophilic and enable the seed to imbibe water at higher tensions. There is higher hydrolytic activity in the pretreated seeds (8). An increase of 25 % over the controls was obtained in grain yield per acre in plots sown with

pretreated seeds (7). This aspect has been discussed in greater details in another paper by us (28).

During the course of last 30 years the extensive work has been carried out on physiology of drought resistance and it is concluded that temperature of ripening period was of paramount importance in determing yield and 1000-kernel weight both under irrigation and water stress conditions. Temperature of drought period has also a profound effect on survival values as well as growth and yield after recovery from wilting. Drought of short is beneficial in the early stages of the plant as far growth and yield are concerned, while drought in the later stages during flowering or maturation adversely affects the growth and yields. Pretreatment of seeds with ascorbic acid helps significantly in over-coming the adverse effect of drought. Early varieties generally escape drought. Properties of protoplasmic colloids such as hydrophily and permeability of protoplasm increased during hardening (8, 16).

Effect of photoperiodic treatments on pods and yield of sesame as well as effect of various chemicals including ascorbic acid on yield of sesame are being investigated in greater details (11). IAA, IBA, and NAA had promotive effects on *Brassica campestris* (6) but they inhibited the process of vernalisation in case of *Linum* (4). None of the auxins tried could produce earliness in flowering when unsplit seeds of *Sesamum indicum* were used for sowing (5).

Thus from the foregoing it is clearly evident that now various parameters are available to select drought resistant varieties as well as in further improving the yield of oilseed crops.

3. **Genetic factors :** According to all experience to date (26) selection for high oil conent can be made without undesirable secondary effects upon seed yield, and the selection for oil can be fairly strong. By selecting for high oil content in several unrelated populations, crossing the selected populations and repeating the selection, it should be possible to counteract the deleterious effects of inbreeding and to accumulate genes for high oil content in the population. The quality of rapeseed oil would be improved considerably if fatty acid pattern is changed through breeding. As linolenic acid is the main precursor for 'off-flavours' (2) in rancid rape seed

oil, it is an important task to diminish the content of this acid. The plant breeder has to dry to increase linoleic acid if this oil has to compete in the market with the cotton oil. The erucic acid should be diminished. Erucic acid with high its high solidification point prevents the use of rapeseed oil as cooking oil. The content of isothiocyanates should also be lowered. When breeding for less tendency towards rancidity, it would be profittable to investigate—in addition to the stability of linolenic acid, free ions of copper and iron and content of vitamin E (tocopherol) (2).

In case of groundnut drought resistant varieties are now available TMV–1 (spreading variety with 135 days duration) and TMV–3 is similar popular type in rainfed areas. This early variety escapes drought periods in later stages of growth and development and hence do well. Spanish–5, Improved Spanish or Improved small Japan are also early varieties (90–105 days). Similarly in case of brown sarson var. DS 17M (Suphala). The greatest difficulty in *Brassica* spp. is that they are very susceptible to mustard aphids and losses due to aphids are enormous. We have to breed varieties, which are resistant to aphids. In this connection, mention may be made here of *Brassica hirta*, which is highly tolerant to mustard aphids, it is higher yielder but being a late variety, it is not preferred (31). It may be mentioned that in case of castor, a very early variety has been developed from variety HC–6; variety 'Aruna' matures in 130–140 days depending upon season through the use of thermal neutrons. The life cycle has been reduced further by nipping all axillary buds of main shoot soon after the emergence of primary spike, without reduction in yield. Nipping resulted in reduced plant height, and effective photosynthetic efficiency. So in case of *B. hirta* similar thermal neutrons may be tried to yield early variety. Physiological manipulations of Photoperiodic and vernalization treatment and use of growth substances may also produce interesting results.

4. Storage factors : Firstly the storage conditions in our country are far from satisfactory and due to faulty and poor storage facilities the losses are quite alarming and as such storage problem is quite complex in case of fatty seeds, because their quality will decrease more or less rapidly depending both upon their chemical composition and to the extent to which they are exposed to air, light and heat. The properties of crude

rapeseed oil—besides its fatty acid composition are in many way dependent upon the degree of maturity of seed, the way of harvesting and drying and storage conditions (2). When the unsaturated fatty acids are attacked by oxygen they undergo a series of reactions at their double bonds and bad tasting even toxic-split products will accumulate. There are larger differences in the rate of oxidation of mono to polyunsaturated fatty acids than those due solely to their number of double bonds. Thus even the saturated fatty acids are oxidized but by another mechanism than the unsaturated ones. The rate of deterioration is however not only dependent upon the fatty acid composition, but also upon some other substances, which are dissolved in the fat. Thus uncomplexed heavy metal ions, mainly copper and iron in native fats increase the rate of oxidation. Vitamin E (tocopherol) and chlorophyll (when fat is kept in light) are native anti-oxidants or pro-oridants. They delay the oxidation of fat at expense of their own oxidation (2). Various workers have worked out best storage conditions of oilseed crops, which we may use:

1. *Arachis hypogaea* seeds if stored at–18 °C or 1 °C give 100 % germination even after 4 years (27); if seeds of groundnut are stored in air tight containers over 4 years, there was still good germination % (24).
2. Seeds of *Brassica napus* var. *napobrassica*, if stored at 4 % moisture in air-tight containers at room temperature retain viability even for 10 years (34); while seeds of *Brassica napus* stored in closed bottles were good even after 5 years (33); and *B. campestris* seeds stored in warehouse retained 50 % germination during 7–11 years storage period (17).
3. *Linum* seeds stored at 7–8 % moisture level in metal containers at 28.9 to 32.2C retained 89–99 % germination after 7–14 years and during their storage for 15–18 years per cent germination was 50–89 % (12); Treated seed, low R. H. and moderate temp. could retain viability for 3.5 years (3).
4. Viability in case of *sesamum* was retained for a period of about 3 years by keeping seeds in air-tight containers (24).

Thus it will be seen from the facts mentioned above that by storing the seeds of various oilseed crops, we can preserve the seeds or germplasms

for a longer period than at the present. Further work is required to intensify researches on various other storage methods and methods for determining viability. The storage and viability. methods should be cheap, reproducible and quick ones.

5. **Plant protection factors :** Although general and specific measures are available now for fungal and viral control of diseases of sesame, linseed, groundnut and *Brassica*, but due to their high cost, non-availability to workers; residual effects, the total measures have been thus still unsatisfactory and hence greater efforts are needed to screen more easily available, cheap, and safer fungicides for effective control of various diseases of these crops (1) Similar is the case with entomological measures. We have to pay attention to newer and safer insecticides like Malathion (safest insecticide); Menazone against aphids; Thiodan and Dipterex against caterpillars and general use rather than DDT etc., whose hazards and residual effects are very well known these days. So we should intensify researches on these safer insecticides very thoroughly on these crops (29). We may try the biological controls also.

Conclusion

One can conclude from the foregoing that it will not possible to add new acreage to the oilseed crops in view of their subsidiary importance and maximum land under cultivation. What we have to do now is to improve these crops at plant types and plant levels only through genetic engineering and physiological manipulations. We should aim at developing early maturing plant types with efficient photosynthesis, resistant to drought, pests and diseases. At plant level further improvement can be done by Physiologist, Pathologist as well as Entomologist. We should aim at having early maturing variety in case of *Brassica*, with lower linolenic acid, erucic acid and isothiocyanates along with higher linolenic acid, Vitamin-E, and lesser amounts of metal ions of copper and iron in oil. Logging resistant varieties need to be developed in case of *Sesamum*, Rainfall and soil types studies have to be conducted very thoroughly for groundnut; Linseed variety should be resistant to pests and diseases. Bunch varieties of groundnut may be sprayed with inhibitors like maleic hydrazide, NAA, coumarin and cycocel etc. to check pre-germination sprouts during harvest. Methods for storage and viability need to be intensified.

The yields of the oilseed crops can be increased to a large extent by the foliar or pretreatment of seeds with ascorbic acid and other growth regulators. Thus various problems of slow progress in increasing productivity in oilseeds crops can be solved to a greater extent by having coordination between different disciplines.

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OPTICAL RESOLUTION OF PARTIALLY ACTIVE (+) PHENYL (2-METHYL) BUTYL CARBINOL AND ITS ALKYL-OXYGEN FISSION REACTIONS

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Summary

Much less work has been done on optically active secondary carbinols with an additional asymmetric carbon atom. The present work, therefore, was undertaken to study the effect on optical rotation by resolving the partially optically active (+) phenyl (2-methyl) butylcarbinol through the newly created secondary -OH group.

Alkyl-oxygen fission reactions were also studied.

Discussion

Kenyon and Pickard have resolved a large number of secondary carbinols of different types [1-9]. These have only one asymmetric carbon atom. In the present work the partially optically active (+) phenyl (2-methyl) butylcarbinol $[\alpha]_D^{32} + 6.48$ ($1=1$) was taken for resolution in which an additional asymmetric carbon atom was created. This carbinol was prepared from (—) 2—methyl-butan-1-ol, $[\alpha]_D^{30} — 4.69$. ($1=1$) as follows :

$$CH_3{\cdot}CH_2{\cdot}\underset{\substack{|\\CH_3}}{CH}{\cdot}CH_2{\cdot}OH \xrightarrow{\text{P (red) and } Br_2} CH_3{\cdot}CH_2{\cdot}\underset{\substack{|\\CH_3}}{CH}{\cdot}CH_2{\cdot}Br$$

(—) 2-methyl-butan-1-ol → (+) 1-bromo-2-mothylbutane

$$\xrightarrow{\text{Mg in Ether}} CH_2{\cdot}CH_2{\cdot}CH{\cdot}\overset{\substack{CH_3\\|}}{C}H_2MgBr \xrightarrow{C_6H_5CHO} CH_3{\cdot}CH_2{\cdot}\overset{\substack{CH_3\\|}}{CH}{\cdot}\overset{\substack{OH\\|}}{CH_2}{\cdot}C_6H_5$$

(+) Phenyl-(2-methyl) butylcarbinol.

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This carbinol showed $[\alpha]_D^{32}$ +6.48 (1=1)

Taking the advantage of the newly created secondary—OH group, the partially optically active hydrogen phthalate was prepared and an attempt was then made to resolve using different alkaloids like l—brucine, l—strychnine and l—quinidine. Out of these l—brucine was found to be more satisfactory. Owing to the resolution through this new centre the carbinol showed high optical rotation as

$[\alpha]_D^{32}$—22.85 (1=1; c, 13.8 in acetone) and

$[\alpha]_D^{32}$+2.32 (1=1, c, 12.5 in acetone)

Experimental

(+) 1-Bromo-2-methylbutane.

The fusel oil containing (—) 2—methyl butan—l—ol was distilled at 128—130° using 16″ long fractinating column, whereby pure (—) 2-methyl butan—1—ol was obtained.[10]

$[\alpha]_D^{32}$—4.69 (1=1); d_4^{30} 0.8279; n^{30} 1.45

(+) 1—Bromo—2—methylbutane was obtained by reacting (—) 2—methyl butan 1—ol (320.0 gm) with red phosphorous (20.0gm) and liquid bromine (266.6 gm). The resulting (+) 1—bromo—2—methylbutane was distilled at 116—118°.[11]

$[\alpha]_D{}^{30}_4$ 1.52 (1=1); d_4^{30} 1.258; n^{30} 1.4580

Partially optically active (+) phenyl (2-methyl) butylcarbinol.

1—bromo—2—methyl butyl—magnesiumbromide was obtained from 1—bromo—2—methylbutane (75.5 gm), Mg turnings (12.16 gm) and ether. It was cooled to 0—5° and the etherial solution of benzaldehyde (53.0 gm) was slowly added during one hour. The complex was refluxed for one hour and kept overnight. Next day it was decomposed with ice and ammonium chloride (10%) solution. The etherial layer was separated, washed with sodium bisulphite (10%) solution, water and dried $(MgSO)_4$. After removal of ether the residual carbinol was obtained at b.p. 216-222°/15 mm. Yield 61.3%.

$[\alpha]_D^{30}$+6.48 (1=1); d_4^{30} 0.9988; n^{30} 1.508

Resolution

Hydrogen phthalate from partially optically active (+) phenyl– (2–methyl) butylcarbinol :

A mixture of partially optically active (+) phenyl–(2–methyl) butylcarbinol, (35·6 gm), benzene (50·0cc), pyridine (30·0cc) and phthalic anhydride (29·6 gm) was refluxed for six hours and kept at room temperature for three days.

The contents were taken in a little acetone and ether (50.0cc) and then washed with HCl (3N), water and dried (sodium sulphate). The hydrogen phthalate, obtained after removal of ether was crystallised from ligroin, m.p. 127–128°; yield 58.6%.

Brucine salt from hydrogen phthalate :

Brucine (39.2 gm.) was slowly added to the partially optically active hydrogen phthalate (32.6 gm.) in acetone (400.0cc), whereby less soluble brucine salt separated which was filtered off and again subjected to four fractional crystallisations in acetone giving brucine salt. m.p. 223–225°.

(–) phenyl (2–methyl) butylcarbinol :

The less soluble brucine salt (10.0 gm.) was decomposed with ice-cold sulphuric acid (3N) to give(–) hydrogen phthalic ester, which was crystallised from ligroin, m.p. 123–124°, $[\alpha]^{32}_{D}$ — 18.32(**l**=1; C, 3.486 in benzene). The rotation of the hydrogen phthalic ester which was $[\alpha]^{32}_{D}$ — 18.32 in acetone, racemised completely on leaving overnight. To the sodium ethoxide solution (Na metal, 3 gm. and 60 ml. ethanol; 99.5%), (–) phenyl (2–methyl) butyl hydrogen phthalate was added and the contents were refluxed for two hours and cooled, extracted with ether, washed with water, dried (sodium sulphate) and on evaporation of the ether yielded the active carbinol.

$(\alpha)^{32}_{D}$ — 22.85 (l=1; c, 13.8 in acetone). It was an oil.

found C, 79.6; H, 9.2

$C_{12}H_{18}O$ Requires C, 80.9; H, 10.1

(+) phenyl (2–methyl) butylcarbinol :

The more soluble brucine salt from the filtrate on slight concentration and decomposition gave partly active (+) hydrogen phthalate,

(14.0 gm.) m.p. 115–116° which subsequently was decomposed with sodium ethoxide to get the partially optically active (+) phenyl (2–methyl) butylcarbinol. $[\alpha]^{32}_{D}$ +2.32 (l=1; c, 12.5 in acetone).

Alkyl—Oxygen Fission Reactions :

(1) (a) Sulphone from partially active (+) phenyl (2–methyl) butylcarbinol :

Partially active carbinol (1.0 gm.) in glacial acetic acid (5.0 ml.) was added to sodium–p–toluene sulphonate (1.5 gm. in 4.0 ml. gla. acetic acid) to which a few drops of con. sulphuric acid were added. On keeping overninght, a white crystalline compound was separated and this was filtered. (0.9 gm.) m.p. 129–130°.

(b) Sulphone from partially active (+) phenyl (2–methyl) butyl hydrogen phthtalate :

The hydrogen phthalate of partially active (+) carbinol (1.8 gm.) was dissolved in NaOH (18 cc; 3N) and to this was added sodium–p–toluene suphonate (1.5 gm.) dissolved in water (20.0 ml). On keeping overnight a white crystalline compound was obtained. (0.8 gm) m.p. 130–131°.

(–) Hydrogen phthalate $[\alpha]^{32}_{D}$ –18.32 (l=1) similarly yielded the (±)–sulphone m.p. 130°.

(2) Phenyl (2–methyl) butyl chloride :

Partially active (+) carbinol (1.0 gm) was triturated with acetyl chloride (1.0cc) and kept in a desiccator for several days over NaOH during which time the colour changed to a dark green brown.

Found Cl 17.61%

$C_{12}H_{17}Cl$ Requires Cl 18.06%

The (–) phenyl (2–methyl) butylcarbinol gave (±) chloride.

(3) Phenyl (2–methyl) butylamine and its derivatives :

Phenyl (2–methyl) butyl hydrogen phthalate (1.8 gm) was dissolved in ammonium hydroxide (50.0cc) and allowed to stand at room temperature for 10 days when a colourless oil was separated, which did not crystalise even on keeping for a long time.

(4) Benzoyl derivative of Phenyl (2-methyl) butylamine :

The oil from (3) (0.5 gm) was shaken with benzoyl chloride (1.0 cc) and NaOH solution (5.0 ml; 3N) The gummy solid separated, was dissolved in ethanol and the solution on cooling gave a white solid. m.p. 158°.

Found N, 4.36%

$C_{19}H_{23}NO$ Requires N, 4.98%

(5) Acetyl derivative of phenyl (2-methyl) butylamine :

The oil from (3) was refluxed for 5-10 minutes with acetic anhydride. On pouring the mixture on ice a white solid mass was obtained, which did not crystallise from benzene, acetone, on alcohol. m.p. 136°.

Found N, 5.9%

$C_{14}H_{21}NO$ Required N, 6.4%

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INHIBITION OF THE CORROSION OF COPPER IN NITRIC ACID

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Abstract

Phenyl hydrazine, hydrazine hydrate, sodium sulphite, sodium bisulphite, and sodium perborate have been investigated as corrosion inhibitors for copper in nitric acid. Phenyl hydrazine and hydrazine hydrate are excellent inhibitors where as the performance of sodium sulphite, sodium bisulphite and sodium perborate is less satisfactory.

The corrosive attack of nitric acid on copper is mainly due to the nitrous acid formed by the reaction between copper and nitric acid. The reaction of nitric acid on copper is conditioned by (1) concentration of the acid; (2) temperature; (3) presence of nitrous acid and (4) solubility of the reaction products in the acid. It has been suggested that as soon as a trace of NO_2 has been formed by the reaction $NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$, it is quickly reduced to NO_2^- by the reaction $NO_2 + e \rightarrow NO_2^-$. Then NO_2^- combines with hydrogen ions to give nitrous acid. Nitrous acid can readily react with nitric acid to regenerate twice the original quantity of NO_2 by the reaction $HNO_2 + HNO_3 \rightarrow 2HNO_2 + H_2O$. In each cycle, the quantity of NO_2 and HNO_2 is doubled. Any substance which can break the catalytic cycle is capable of retarding the corrosion of copper in nitric acid. Aromatic amines can react with nitrous acid to form diazo compounds and thus act as inhibitors.

The present article reports the use of phenyl hydrazine, hydrazine hydrate, sodium sulfite, sodium bisulfite and sodium perborate as corrosion inhibitors for copper in nitric acid.

Experimental :

Electrolytic copper supplied by Kamani Metals and Alloys Ltd., Bombay were used for the study. The preparation of specimens and corrosion tests were carried out as described in our earlier publication[1].

The influence of time and nitric acid concentration on inhibitor efficiency is given in Table 1. The change in potential of copper with time in 2.0 N nitric acid in the presence and absence of inhibitors is given in figure 1. The effect of current density on the cathode and anode potentials of copper in 2.0N nitric acid in the presence and absence of inhibitors is given in figure 2. The dissolution of copper in nitric acid increases with time as well as with the concentration of nitric acid. The steady state potential value of copper in 2.0N nitric acid is +22 mv. The value of i_{corr} in 2.0N nitric acid is 1.549×10^{-3} amp/cm^2.

In order to estimate the influence of an inhibitor, it is very important to measure the loss in weight of metal in the first few minutes of the reaction and this is especially true for the aggressive media. According to Putilova[2], insufficient attention is being given in studying the initial period of the corrosion of metals in the presence of various inhibitors, which could partly explain the lack of agreement often observed between results of laboratory tests and practical conditions.

Phenyl hydrazine :

Phenyl hydrazine is a good inhibitor. It is relatively more effective in concentrations of nitric acid above 2.0N. The corrosion of copper in 3.0N nitric acid for 15–60 minutes in the presence of 2.17–17.4 ml/1 of phenyl hydrazine is less than that in 2.0N nitric acid. Such a behaviour is also observed in 4.0N and 5.0N nitric acid solutions for 10–30 minutes duration.

In 4.0N and 5.0N nitric acid, even at as low a concentration as 2.17 ml/1 of phenyl hydrazine, the corrosion of copper is retarded to an extent of 97–99%, whereas in 2.0N and 3.0N, it is retarded to an extent of 83–94% and 93–99% respectively.

The steady state potential of copper in 2.0N nitric acid in the presence of 17.4 ml/1 phenyl hydrazine shifts slightly in the positive direction, the value being +28 mv.

There is considerable cathode polarization as compared to the anode polarization. Thus, the effect of phenyl hydrazine is of a mixed type with a predominant action on local cathodic areas.

The value of i_{corr} is $4 \cdot 677 \times 10^{-5}$ amp. / cm² the efficiency being 97.0%.

Hydrazine hydrate :

Hydrazine hydrate is a very good inhibitor for copper in nitric acid. The inhibitive action of hydrazine hydrate is immediate and it is highly effective in 2.0–4.0N nitric acid at 0.43 ml/l concentration of hydrazine hydrate, whereas in 5.0N nitric acid. the effective inhibition is obtained at higher concentration, 0.87 ml/l of hydrazine hydrate. The loss in weight of copper in 2.0N, 3.0N, 4.0N and 5.0N nitric acid solutions for the period of 15 minutes at 0.87 ml/l of hydrazine hydrate, is respectively 1.3, 1.4, 1.7 and 1.1 mg/dm². Even though the corrosive power of 2.0N, 3.0N, 4.0N and 5.0N nitric acid differ to a great extent, the effect of nitric acid concentration is not felt in the presence of hydrazine hydrate.

The addition of inhibitor shifts the steady state potential in the negative direction, the value being —42 mv, indicating the predominant action of hydrazine hydrate on the cathodic reaction.

Upto the current density 4.872×10^{-3} amp./cm², the cathode polarization is significant but beyond this current density, the shift in the cathode potential is less than that in 2.0N nitric acid alone, e.g., at the current density of 1.461×10^{-2} amp./cm², the shift in cathode potential during cathode polarization is (272–42) 230 mv, whereas the corresponding shift in 2.0N nitric acid alone is (245+25) 270 mv. From the polarization results, it appears that hydrazine hydrate is of a mixed type of inhibitor and increases the polarization of both the cathode and anode, the cathode polarization is to a greater extent as compared to the anode polarization. The value of i_{corr} is 6.310×10^{-6} amp./cm², the efficiency being 99.6%.

Sodium sulphite :

Sodium sulphite is effective in dilute nitric acid solutions and the effective inhibition is obtained at lower concentration of sodium sulphite as compared to that in concentrated nitric acid solutions. Thus, in 2.0N nitric acid, 0.2% concentration of sodium sulphite is effective. Whereas in 3.0N nitric acid the effective inhibitor concentration is 2.0%. 1%

concentration of sodium sulphite is effective in 3.0N nitric acid only for a period of 10 minutes, after which, the efficiency decreases remarkably. Lo ≰ er concentrations of sodium sulphite accelerate the corrosion o copper in nitric acid solutions. In 2.0N nitric acid, the corrosion of copper is accelerated at 0.01% of sodium sulphite whereas in 3.0N nitric acid, the corrosion of copper is accelerated in the presence of 0.1–0.5% concentrations of sodium sulphite. In 4.0N and 5.0N nitric acid solutions, sodium sulphite is not at all effective. Probably, sodium sulphite acts as inhibitor by decomposing nitrous acid.

$$3HNO_2 + 2Na_2SO_3 \rightarrow 2NaNO_2 + H_2O + Na_2HNS_2O_7.$$

Sodium bisulphite :

The corrosion of copper is effectively retarded in 2.0N nitric acid at 0.5 % concentration of sodium bisulphite, the inhibition being 99.9%. At concentrations lower than 0.5%, the efficiency decreases with time. As the concentration of nitric acid is increased, the inhibition is obtained at higher concentrations of sodium bisulphite. Thus, in 3.0N nitric acid, 87–98% inhibition is obtained at 2% concentration of sodium bisulphite. In 2.0N nitric acid, the corrosion of copper is accelerated in the presence of 0.01% sodium bisulphite. The acceleration of the corrosion of copper at lower concentrations of sodium bisulphite is more evident in 3.0N nitric acid solutions. Sodium bisulphite is useless as an inhibitor in 4.0N and 5.0N nitric acid solutions.

Sodium perborate :

In 2.0 N nitric acid, the corrosion of copper is retarded to an extent of 89–97% at 0.2% concentration of sodium perborate. With further increase in the concentration of sodium perborate, the efficiency decreases. In 3.0N nitric acid, the corrosion of copper ts retarded effectively for 10 minutes at 0.5% concentration of sodium perboıate and beyond 0.5% concentration of the inhibitor, the efficiency decreases. During 15 to 60 minutes period, the optimum concentration of sodium perborate is 1% and beyond which, the protective power falls off. In 3.0N nitric acid, even at the optimum concentration the efficiency decreases with time whereas in 2.0N nitric acid, it increases with time. In 3.0N nitric acid, there are strong instances of the acceleration of the corrosion of copper at lower

concentrations of sodium perborate. Sodium perborate is not at all effective in 4.0N and 5.0N nitric acid solutions.

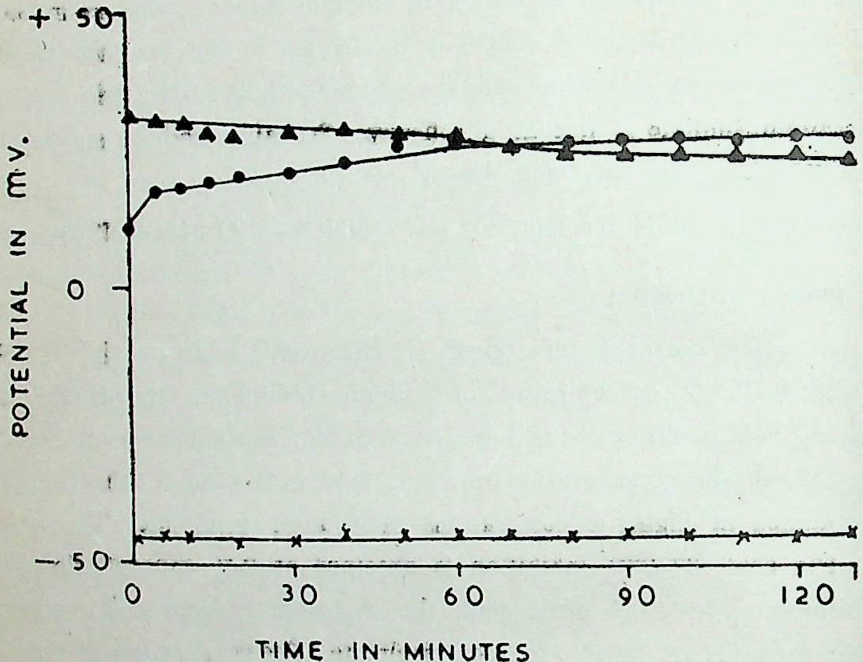

Figure 1 : Change in potential of copper with time in 2.0N nitric acid in the presence and absence of inhibitors

△ phenylhydrazine

× hydrazinehydrate

● 2.0N HNO_3

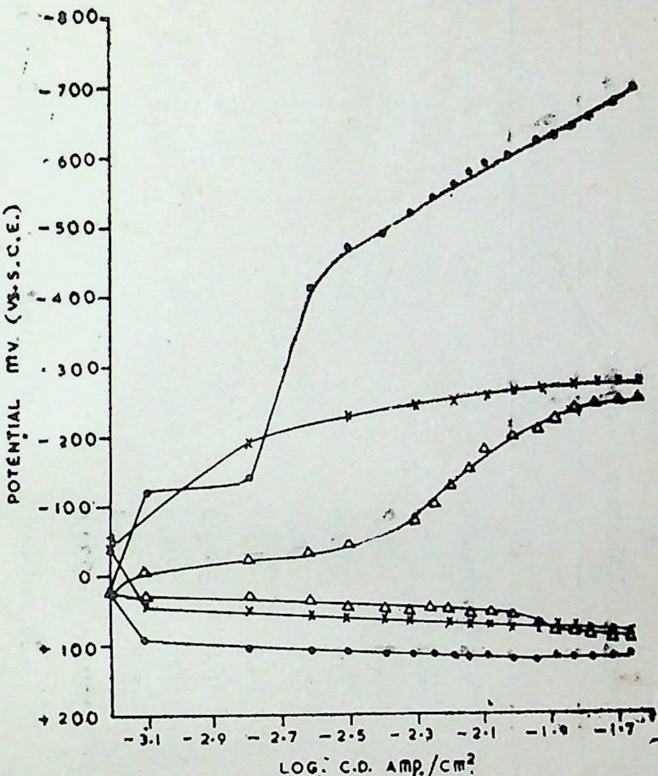

Figure 2 : Influence of current density on the cathode and anode potentials of copper in 2.0N nitric acid in the presence and absence of inhibitors

● phenylhydrazine

× hydrazinehydrate

△ 2.0N HNO_3

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TABLE 1

Performance of Inhibitors in Nitric Acid

Inhibitor	*Inhibitor concen.%*	*$loss_2$ mg/dm*	*% Efficiency*	*$loss_2$ mg/dm*	*% Efficiency*	*$loss_2$ mg/dm*	*% Efficiency*	*$loss_2$ mg/dm*	*% Efficiency*
1	2	3	4	5	6	7	8	9	10
1.0N HNO_3		**60 minutes**		**100 minutes**					
	nil	23.8	–	48.2	–				
Phenylhydrazine	2.17 ml/1	9.5	60.1	11.4	76.3				
	4.35 ,,	8.3	65.1	8.3	82.8				
	8.7 ,,	2.8	88.2	2.8	94.2				
Sodium sulphite	0.001 %	24.9	–4.6	54.6	–13.3				
	0.010 %	23.5	+1.3	46.0	+4.6				
	0.20 %	0.5	97.9	0.8	98.3				
Sodiumperborate	0.20 %	17.2	27.7	17.3	64.1				
	2.0 %	78.7	–230.7	159.5	–231.0				
2.0N HNO_3		**15 minutes**		**30 minutes**		**60 minutes**		**120 minutes**	
nil		77.0	–	154.6	–	314.7	–	1318.0	–
Phenylhydrazine	2.17 ml/1	13.3	82.7	21.7	86.0	36.8	88.3	67.9	94.7
	4.35 ,,	12.2	84.2	19.7	87.3	29.1	90.7	56.2	95.8
	8.70 ,,	11.4	85.2	16.9	89.1	25.8	91.8	50.7	96.1
	17.4 ,,	–	–	11.9	90.3	16.9	94.6	23.3	98.3
Hydrazine hydrate	0.43 ml/1	2.2	97.1	3.3	97.9	3.9	98.4	8.6	99.4

	17.4 ,,	–	–	11.9	90.3	16.9	94.6	23.3	98.3
Hydrazine dydrate	0.43 ml/1	2.2	97.1	3.3	97.9	3.9	98.4	8.6	99.4
	0.87 ,,	1.3	98.3	2.2	98.6	3.3	99.0	7.8	99.5
Sodium sulfite	0.01 %	84.2	–9.3	166.3	–7.6	–	–	–	–
	0.20 %	0.3	99.6	0.5	99.8	0.8	99.7	0.8	99.7
Sodium bisulfite	0.01 %	94.2	–22.3	137.3	–14.7	350.1	–11.2	962.5	27.6
	0.10 %	0.5	99.4	0.5	99.7	120.5	61.7	241.8	81.7
	0.20 %	0.5	99.4	0.5	99.7	0.5	99.8	90.8	93.2
	0.50 %	–	–	–	–	–	–	0.5	99.9
Sodium perborate	0.2 %	8.0	89.6	13.3	93.3	22.7	92.8	43.2	96.7
	2.0 %	30.5	60.4	46.8	69.7	71.7	77.2	139.1	89.4
3.0N HNO_3		**10 minutes**		**15 minutes**		**30 minutes**		**60 minutes**	
nil		113.8	–	202.2	–	703.6	–	3075.5	–
Phenylhydrazine	2.17 ml/1	6.1	94.6	6.1	97.0	6.4	99.1	7.5	99.8
	4.35 ,,	5.3	95.3	6.1	97.0	6.1	99.1	6.9	99.8
	8.70 ,,	5.0	95.6	5.3	97.4	5.5	99.2	6.4	99.8
	17.4 ,,	4.7	95.8	5.0	97.5	5.0	99.3	5.0	99.8
Hydrazine hydrate	0.43 ,,	0.5	99.9	0.8	99.9	1.7	99.7	2.2	99.9
	0.87 ,,	0.5	99.9	0.8	99.9	1.7	99.7	2.2	99.9
Sodium sulfite	0.10 %	284.5	–150.0	624.1	–208.6	–	–	5540.0	–80.7
	0.20 %	268.8	–136.0	482.5	–138.7	2088.0	–196.7	5540.0	–80.7
	0.50 %	–	–	–	–	–	–	5540.0	–80.7
	1.0 %	0.8	99.3	142.9	29.3	264.5	62.4	2331.0	24.2
	2.0 %	0.5	99.5	0.5	99.7	0.5	99.9	1.4	99.9

1	2	3	4	5	6	7	8	9	10
Sodium bisulfite	0.5%	310.6	–172.2	512.5	–153.5	–	–	2582.0	15.9
	1.0%	–	–	512.5	–153.5	–	–	2000.0	35.0
	2.0%	1.7	98.5	25.7	87.3	37.7	94.6	80.6	97.4
4.0N HNO_3		**2 minutes**		**5 minutes**		**10 minutes**		**15 minutes**	
Nil		123.3	–	1066.4	–	2434.8	–	3938.4	–
Phenylhydrazine	2.17 ml/1	2.2	98.2	7.8	99.3	16.9	99.3	45.1	98.9
	26.1 ,,	0.0	100.0	0.0	100.0	9.7	99.6	21.9	99.4
Hydrazinesulfate	0.43 ,,	0.3	99.7	0.5	99.9	0.8	99.9	1.7	99.7
	0.87 ,,	0.3	99.7	0.5	99.9	0.8	99.9	1.7	99.7
5.0N HNO_3		**2 minutes**		**5 minutes**		**10 minutes**		**15 minutes**	
Nil		845.8	–	2046.0	–	3834.0	–	5838.0	–
Phenylhydrazine	2.17 ml/1	4.7	99.4	10.5	99.5	169.0	99.5	25.6	99.5
	26.1 ,,	1.2	99.9	6.0	99.6	6.9	99.8	18.8	99.7
Hydrazinesulfate	0.87 ,,	0.3	99.9	0.8	99.7	1.1	99.9	1.1	99.9

INHIBITION OF THE CORROSION OF 63/37 BRASS IN ACETIC ACID AND PHOSPHORIC ACID

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Abstract

Furfuraldehyde and cyclohexanone have been investigated as corrosion inhibitiors for 63/37 brass in acetic and phosphoric acid solutions.

For acetic acid and other hydroxy acids in quiet room temperature exposure, corrosion rates of copper-zinc alloys run down to 10 to 100 mg/dm^2/day. Agitation, aeration and elevated temperatures push the rates up into 50–600 mg/dm^2/day[1].

Uhlig[2] reports that in quiet solutions at room temperature with limited aeration corrosion rates of copper and zinc alloys range from 0.0001 to 0.030 ipy. however, increased aeration and elevated temperatures increase the corrosion hundred–fold. Movement of acetic acid relative to brass surface also enhances corrosion. At room temperature, 80% crude acetic acid attacks brass to an extent of 7 to 10 mpy whereas in 80% pure acetic acid the corrosion rate of brass is 12 to 15 mpy at the bottom of the tank but 83 to 105 mpy at the top of the tank[3]. The corrosion rate of brasses in acetic acid were studied by Dujjin[4] who reported that 70/30 brass shows highest corrosion resistance. Bosworth[5] and Eisenbrown[6] also studied the corrosion of brasses by acetic acid in combination with various other liquids. Stillwell[7] and Turnipseed followed the corrosion of Σ–brass in acetic acid by X–ray diffraction method and

observed that acetic acid preferentially dissolves zinc which results in successive formation or γ–brass, β–brass, α–brass and copper.

Desai and Trivedi[8] reported that even though acetic acid is a weak acid it is highly corrosive to brasses. Oxygen solubility plays a significant role in corrosive action of acetic acid. Moreover, the high corrosivity may also be due to complex formation as suggested by Bengough and May. Talati[9] reported that the extent of corrosion of 80/20 brass and 59/41 brass is practically the same. 80/20 brass dissolves as a whole unit, but 59/41 brass shows dezincification at all concentrations of acetic acid. This tendency is more remarkable in dilute solutions. He further reported that glacial acetic acid is highly corrosive to brasses and 60/40, 70/30 and 80/20 brasses dissolve as a whole unit in it. The order of corrosive attack of glacial acetic acid for various types of brasses for 1 to 4 weeks duration is $60/40 > 80/20 > 70/30$.

Pure phosphoric acid in the cold and low rate aeration is well resisted by copper alloys with rates ranging below 100 mg/dm^2/day.[1] High temperatures push the corrosion rates into several thousand mg/dm^2. Laque and Copson[3] reported that the corrosion rates of copper zinc alloys range from 22–73 mpy. Uhlig[2] states that the corrosion rates of brasses in pure phosphoric acid at room temperature range from 0.001 to 0.2 ipy depending on the degree of aeration. Raising the temperature increases the corrosion rate from tenfold to hundred fold. The presence of oxidising agents increases the corrosion rate appreciably. Sanfourche[10] studied the corrosion of brasses containing 60-65% copper in phosphoric acid and observed that the constituents are dissolved in the same proportion as they are present in the alloy. Desai and Trivedi[8] observed that phosphoric acid is not corrosive towards 60/40 and 67/33 brasses at 0.001N concentration. However, at higher concentration of the acid it is highly corrosive. At 0.1N concentration, the corrosion of brass is maximum indicating the importance of

oxygen in controlling the corrosion. Talati[9] reported the corrosion rates of 80/20 and 59/41 brasses in phosphoric acid solutions.

Experimental :

63/37 brass supplied by M/s. Kamani Metals and Alloys, Bombay, was used for the experiments. The preparation of specimens (6cm × 3cm thickness 28 S.W.G.), corrosion tests and cleaning of the specimens after corrosion were carried out as described in our previous publications.

The present article reports the use of furfural dehyde and cyclohexanone as corrosion inhibitors for 63/37 brass in acetic acid and in phosphoric acid.

Acetic acid :

The retardation of corrosion of 63/37 brass by the substances studied is shown in table 1. The ratio of copper and zinc going in solution are given in table 2.

Furfuraldehyde is an excellent inhibitor for the corrosion of 63/37 brass in acetic acid. In 0.2–3.0N solutions of acetic acid, its efficiency ranges from 84–92%. The effective inhibitor concentration of furfuraldehyde is 26.1 ml/l. In acetic acid, in general, there is preferential dissolution of copper whereas in the presence of furfuraldehyde there is a slight preferential dissolution of zinc.

The performance of cyclohexanone is less satisfactory than that of furfuraldehyde. It is interesting to note that its efficiency improves as the concentration of acetic acid is increased from 0.5N to 3.0N. In the presence of cyclohexanone, there is preferential dissolution of zinc.

Phosphoric acid :

Preliminary results indicated that cyclohexanone is not a satisfactory inhibitor for 63/37 brass. The performance of furfuraldehyde in phosphoric acid is given in table 3. In phosphoric acid also, furfuraldehyde is a very good inhibitor. It affords satisfactory protection (87–90%) to 63/37 brass in 0.2–2.0N solutions of phosphoric acid. However, in 3.0N phosphoric acid, there is a slight fall in its efficiency. In the presence of furfuraldehyde, there is dezincification of 63/37 brass.

TABLE 1

Corrosion of 63/37 Brass in The Presence of Inhibitors in Acetic Acid
(Values in the bracket show % inhibition)

Duration : 5 days

Temp. : $35 \pm 0.5°C$

Inhibitor	*Inhibitor concn.* ml/1	0.2N	0.5N	1.0N	2.0N	3.0N
Nil	—	139.0 (—)	95.3 (—)	100.0 (—)	188.4 (—)	113.6 (—)
Furfural-dehyde	2.17	88.6 (36.2)	88.6 (7.0)	99.7 (0.3)	108.0 (42.7)	123.0 (-8.2)
	4.35	77.6 (44.2)	78.6 (17.5)	94.5 (5.5)	88.9 (52.8)	100.6 (11.4)
	8.70	49.9 (64.1)	49.0 (48.5)	81.7 (18.3)	70.3 (62.7)	78.1 (31.2)
	17.4	44.8 (67.7)	41.2 (56.7)	72.3 (27.7)	39.9 (78.8)	54.6 (51.9)
	26.1	14.4 (89.6)	14.4 (84.9)	15.2 (84.4)	14.4 (92.3)	16.6 (85.4)
Cyclohexa-none	2.17	72.3 (48.0)	127.9 (-34.2)	99.7 (0.3)	117.1 (37.7)	30.9 (74.0)
	4.35	65.3 (53.0)	95.3 (0.0)	88.6 (11.4)	81.7 (56.9)	29.1 (75.2)
	8.70	62.3 (55.2)	74.2 (22.1)	77.5 (22.4)	50.7 (73.1)	24.4 (78.5)
	17.4	58.7 (57.8)	60.9 (36.1)	53.4 (46.5)	39.3 (79.1)	20.8 (81.7)
	26.1	48.9 (65.0)	49.9 (47.7)	50.7 (49.5)	30.4 (83.8)	9.4 (82.9)

TABLE 2

Copper/Zinc Ratios

	0.2N	0.5N	1.0N	2.0N	3.0N
Acetic acid					
Nil	1.89	2.66	0.92	0.46	0.47
Furfuraldehyde 26.1 ml/1	1.5	1.7	1.6	1.2	1.1
Cyclohexanone 26.1 ml/1	0.85	1.5	1.0	1.5	1.3
Phosphoric acid					
Nil	1.67	0.88	0.77	1.28	0.88
Furfuraldehyde 26.1 ml/1.	1.5	1.0	0.70	0.75	0.88

TABLE 3

Corrosion of 63/37 Brass in The Presence of Inhibitors in Phosphoric Acid

(Values in the bracket show % inhibition)

Duration : 5 days — Temp. : $35 \pm 0.5°C$

Inhibitor	*Inhibitor concn.* ml/1	0.2N	0.5N	2.0N	3.0N
Nil	—	151.0 (—)	176.4 (—)	188.4 (—)	113.5 (—)
Furfuraldehyde	2.17	94.2 (47.2)	83.1 (53.0)	64.2 (67.6)	96.4 (15.0)
	4.35	83.1 (54.4)	56.5 (66.5)	47.1 (75.0)	—
	8.70	47.1 (66.6)	47.1 (73.3)		80.4 (38.1)
	17.4	19.4 (87.1)	19.4 (89.1)	33.5 (82.4)	75.4 (42.6)
	26.1	13.8 (90.6)	13.8 (90.0)	23.0 (87.7)	47.6 (58.3)

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INHIBITION OF THE CORROSION OF COPPER IN LACTIC ACID

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Abstract

Agar, dextrine, gelatine, gumarabic, pyrogallol have been investigated as corrosion inhibitors for copper in lactic acid. All the substances are mixed inhibitors with predominant action on the cathode.

Yakhontov[1] studied the corrosion of copper in lactic acid. Rabald[2] studied the effect of oxygen on the corrosion of metals in organic acids. The rate of corrosion at room temperature for copper in lactic acid and malic acid are of the order of 6–70 mg. per sq. dm. per day. At temperatures upto boiling the rates range upto 120 mg. per sq. dm. per day.[3] The present article reports the use of agar agar, dextrine, gelatin, gumarabic and pyrogallol as inhibitors for the corrosion of copper in lactic acid.

Experimental

Electrolytic copper supplied by Kamani Metals and Alloys Ltd., Bombay were used for the study the preparation of specimens and corrosion tests were carried out as described in our earlier publication.[4]

The effect of inhibitor concentration and time on inhibitor efficiency is given in tables 1 and 2 respectively. The change in potential of copper with time in 0.5N lactic acid in the presence and absence of inhibitors is given in figure 1. The effect of current density on the cathode and anode potentials of copper in 0.5N lactic acid in the presence and absence of inhibitors is given in figure 2.

Lactic acid

With time the potential of copper in 0.5N lactic acid becomes more positive. The steady state potential is—30 mv. The anode polarization is quite negligible but the cathode polarization is considerable. Thus, the corrosion of copper in lactic acid is mainly cathodically controlled.

Agar—agar

At 2% cocentration of agar–agar, the corrosion of copper in 0.2N lactic acid for three days is retarded to an extent of about 81.0%, the corresponding inhibition in 0.5N and 1.0N lactic acid being only about 43%. Agar--agar is more effective throughout during three to nine days in 0.2N lactic acid as compared to that in 0.5N and 1. ON lactic acid. In 0.5N lactic acid for nine days period, at 2% concentration of agar--agar, the corrosion of copper is retarded only to an extent of about 14%. At 2% concentration of agar–agar, the corrosion of copper in 0.2N 0.5N and 1.0N lactic acid is retarded during three to nine days respectively in the range of 59.5%, -80.9%, 14.4%, —62.1%, and 40.8%--50.0%.

The potential values are throughout less negative in the presence of 2% agar--agar as compared to those in 0.5N lactic acid. The steady state to potential is —22mv.

The cathode is considerably polarized in the presence af agar–agar. In the presence of agar–agar the anode polarization is also increased. Thus, agar–agar is a mixed type of inhibitor with predominant action on the lacal cathodic areas.

Dextrin

When the results are compared in 0.2N, 0.5N and 1.0N lactic acid at 2% concentration of dextrin for three, seven and nine days period, the order of efficiency of dextrine is 0.2N > 0.5N > 1.0N lactic acid, however, for five days, the order is 0.5N > 0.2N > 1.0N lactic acid. At 2% concentration of dextrin, the corrosion of copper in 0.2N, 0.5N and 1.0N lactic acid during three to nine days is retarded respectively in the range of 46.4%-67.0%, 32.2%-58.4% and 25.7%- 47.6%. It is interesting to note that in 0.5N lactic acid, the corrosion of copper for five days period is accelerated in the presence of 0.1% dextrin.

In the presence of 0.1% dextrin, the corrosion of copper in 0.5N lactic acid is accelerated to an extent of 16%. In the presence of 0.1% dextrin, the potential values are throughout less negative as compared to those in 0.5N lactic acid alone. Thus, it appears that the acceleration may be due to the cathodic depolarization in the presence of 0.1% dextrin. In the presence of 2%, dextrin, where the corrosion of copper is inhibited to an extent of 56% upto seven days, the potential values shift in the negative direction. This is likely due to predominant action of dextrin on the local cathodic areas. The steady state potential is about-80 mv.

There is considerable cathode polarization in the presence of 2.0% dextrin. The anode polarization has also increased in the presence of 2% dextrin. Thus, dextrin is a mixed type of inhibitor with its Predominant action over local cathodic areas.

Gelatine

For five days period, the corrosion of copper in 0.2N and 1.0N lactic acid in the presence of 0.1% gelatine, is accelerated. In 0.2N, 0.5N and 1.0N lactic acid, at 2% concentration of gelatine, the corrosion of copper for five days period is retarded respectively only to extend of 51.2%, 56.5% and 55%. Gelatine is particularly weak as an inhibitor in 1.0N lactic acid. The efficiency of gelatine falls considerably with time in 1.0N lactic acid.

The potential shifts to more negative direction with the concentration of gelatine. The steady state potential in the presence of 0.1% gelatine is –70 mv whereas that in the presence of 2.0% gelatine is –100 mv. The shift of the steady state potential is in the negative direction on the addition of gelatine indicates its predominant action over local cathodic areas.

In the presence of gelatine both the cathode and anode are polarized, the cathode to a greater extent as compared to the anode. Thus, gelatine is a mixed type of inhibitor with its predominant over local cathodic areas.

Gum-arabic

For five days duration, gum-arabic is more effective in 0.2N and 0.5N lactic acid as compared to that in 1.0N lactic acid, the protection being respectively 65.3%, 65,7% and 48.6%

In the presence of 2% gum-arabic, Gum-arabic being particularly more effective in 0.2N lactic acid as the % efficiency during three to nine days is higher than that observed in 0.5N and 1.0N lactic acid. In 0.5N and 1.0N lactic acid, the efficiency of gum-arabic (2%) drops considerably for nine days duration, thus the efficiency of gum-arabic in 0.5N and 1.0N lactic acid drops respectively from 69.2% to 38.9% and from 58.9% to 43.5%. The corrosion of copper in 0.2N, 0.5N and 1.0N lactic acid in the presence of 2% gum-arabic during three to nine days in retarded respectively in the range 61%–72%, 38.9%–69.2% and 43.5%–58.9%.

The potential values are more negative in the presence of 0.1% and 2.0% gum-arabic as compared to those in 0.5N lactic acid. The shift in the negative direction increases with the concentration of gum-arabic. It appears that the effect of gum-arabic is predominantly over local cathodic areas.

Gum-arabic increases the polarization of both the cathode and anode, the cathode to a greater extent as compared to the anode.

Pyrogallol

The increased corrosion of copper in the presence of 0.1% pyrogallol is quite evident in 0.2N lactic acid, the acceleration being 70.0%. For three days and nine days, the corrosion of copper in the presence of 2% pyrogallol is retarded in the order of 0.2N > 0.5N > 1.0N lactic acid. The corrosion of copper in 0.2N, 0.5N and 1.0N lactic acid in the presence of 2% pyrogallol during three to nine days is retarded respectively in the range 54%–70%, 51%–65% and 43%–63%.

The potential values are more negative in the presence of 2% pyrogallol as compared to those in the presence of 0.1% pyrogallol. In the presence of 2% pyrogallol the corrosion of copper on 0.5N lactic acid is inhibited to a greater extent as compared to that in the presence of 0.1% pyrogallol. Even in the presence of 2% pyrogallol the efficiency decreases considerably after five days, this is also reflected by the fall in potential values.

There is considerable cathode polarization in the presence of pyrogallol. The anode polarization is also increased and the shift in the anode potentials is noteworthy at higher current densities. The pyrogallol is a mixed type of inhibitor with its predominant action over local cathodic areas.

TABLE I

Efficiency (%) of inhibitors in Lactic acid

Duration : 5 days — Temperature : 35°C ± 0.5°C

Inhibitor	Inhibitor concen %	0.2N loss mg/dm²	0.2N % Inhibition	0.5N loss mg/dm²	0.5N % Inhibition	1.0N loss mg/dm²	1.0N % Inhibition
1	2	3	4	5	6	7	8
Agar-agar	0.00	94.2	—	93.6	—	60.9	—
	0.1	69.0	26.8	58.7	37.3	55.4	9.1
	0.2	57.9	38.5	56.2	40.0	50.7	16.8
	0.5	38.5	59.1	54.0	42.3	41.6	31.8
	1.0	31.8	66.2	46.5	50.3	36.3	40.5
	2.0	17.2	81.8	35.5	62.1	30.5	50.5
Dextrin	0.1	89.2	52.9	108.6	-16.0	49.3	19.1
	0.2	67.0	28.8	82.0	12.4	42.9	29.6
	0.5	55.4	41.2	64.3	31.4	40.1	34.2
	1.0	54.0	42.6	54.9	32.9	38.8	36.4
	2.0	49.9	47.1	40.4	56.8	35.7	41.4

1	2	3	4	5	6	7	8
Gelatine	0.1	115.6	–23.0	73.3	21.9	70.4	–15.5
	0.2	75.4	20.0	62.5	33.2	47.9	21.4
	0·5	55.7	40.9	57.6	38.5	33.2	45.5
	1.0	48.7	48.3	49.0	47.6	30.5	50.0
	2.0	46.0	51.2	40.7	56.6	27.4	55.0
Gum-arabic	0.1	73.7	21.7	58.2	37.9	48.2	20.9
	0.2	46.5	50.6	45.1	51.8	40.7	33.2
	0.5	43.8	53.5	37.9	59.5	38.8	36.4
	1.0	40.2	57.4	36.0	61.5	36.0	40.9
	2.0	32.7	65.3	32.1	65.7	31.3	48.6
Pyrogallol	0.1	160.1	–70.0	94.5	–0.9	61.5	–0.9
	0.2	102.0	–8.3	85.6	8.6	52.4	14.1
	0.5	70.1	25.6	77.6	17.1	36.8	39.6
	1.0	60.1	36.2	53.7	42.6	31.6	48.4
	2.0	39.6	57.9	36.6	60.9	22.7	62.7

TABLE 2

Efficiency (%) of Inhibitors in Lactic Acid

Normality of Lactic Acid	Inhibitor	Inhibitor Concen.%	3 days		5 days		7 days		9 days	
			loss mg/dm²	% Inhibition	loss mg/dm²	% Inhibition	loss mg/dm²	% Inhibition	loss mg/dm²	% Inhibition
0.2N	nil	nil	53.7	—	94.2	—	114.7	—	144.3	—
0.5N	nil	nil	47.9	—	93.6	—	119.9	—	129.1	—
1.0N	nil	nil	34.3	—	60.9	—	82.8	—	103.5	—
0.1N	Agar-agar	2.0	10.2	80.9	17.2	81.8	32.7	71.5	58.4	59.5
0.5N		2.0	27.4	42.8	35.5	62.1	60.1	49.8	110.5	14.4
1.0N		2.0	19.7	42.7	30.5	50.0	45.8	44.7	61.2	40.8
0.2N	Dextrine	2.0	17.7	67.0	49.9	47.1	60.4	47.4	77.3	46.4
0.5N		2.0	19.9	58.4	46.4	56.8	68.1	43.2	87.3	32.2
1.0N		2.0	25.5	22.0	31.0	40.8	47.9	30.0	63.2	38.7
0.2N	Gelatine	2.0	22.2	58.8	46.0	51.2	51.8	54.9	74.2	48.5
0.5N		2.0	27.7	42.2	40.7	56.5	45.4	79.6	85.9	46.2
1.0N		2.0	21.8	39.5	27.4	55.0	74.8	9.7	84.5	18.3
0.2N	Gum-arabic	2.0	14.7	72.7	32.7	65.3	44.9	60.9	52.6	63.5
0.5N		2.0	14.7	69.2	32.1	65.7	59.3	43.9	78.9	38.9
1.0N		2.0	14.1	58.9	31.3	48.6	46.3	44.1	58.4	43.5
0.2N	Pyrogallol	2.0	16.3	69.6	39.6	57.9	53.0	53.9	59.3	58.9
0.5N		2.0	21.6	54.9	36.6	60.9	42.4	64.6	63.2	51.1
1.0N		2.0	18.6	46.1	22.7	62.7	44.9	45.8	58.8	43.2

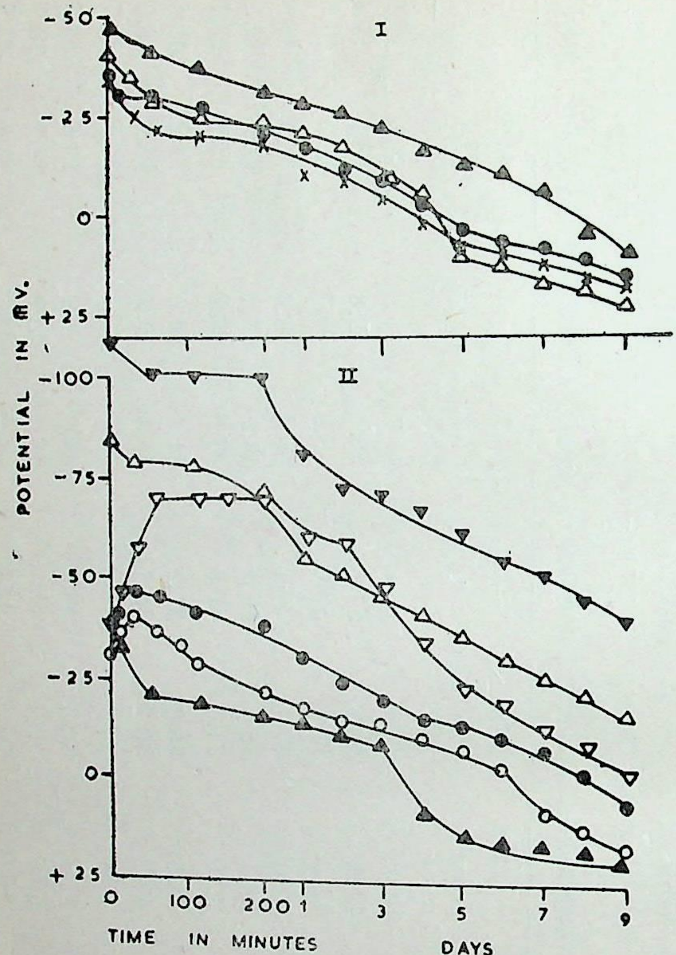

Figure 1 : Change in potential of copper with time in lactic acid in the presence and absence in inhibitors

I ×—× agar-agar
△—△ pyrogallol 0.1 %
▽—▽ pyrogallol 2.0 %
●—● uninhibited lactic acid

II △—△ dextrin 0.1 %
△—△ dextrin 2.0 %
▽—▽ gelatine 0.1 %
▽—▽ gelatine 2.0 %
○—○ gum-arabic 0.1 %
●—● gum-arabic 2.0 %

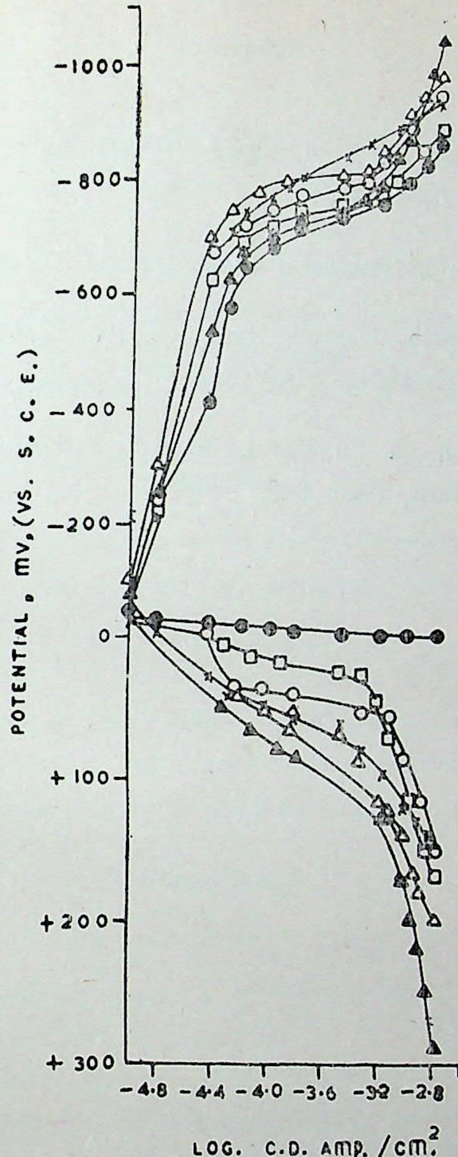

Figure 2 : Influence of current density on the cathode and anode potentials of copper in lactic acid in the presence and absence of inhibitors :

○—○ agar-agar
×—× dextrine
△—△ gelatine
△—△ gum-arabic
□—□ pyrogallol
●—● uninhibited lactic acid

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BENZYLTHIOUREAS PART VI

SYNTHESIS OF 1--ALKOXYBENZYL--2--THIOUREAS

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Summary

4–Alkoxy and 3–methoxy–4–alkoxybenzylthioureas have been prepared by the action of ammonia on corresponding *iso*thiocyanates.

In continuation of our earlier work benzylthioureas containing one or two ether groups on the aromatic ring are described here. These compounds were prepared from alkoxybenzylamines.

Experimental

All melting points are uncorrected.

Alkoxybenzyl *iso*thiocyanates : These were prepared from alkoxybenzylamines as described earlier[1], and are shown in Table I. Alkoxybenzylamines were prepared by reduction of oximes[2]. 4–Alkoxybenzaldehydes were prepared by alkylation of 4–hydroxybenzaldehyde and 3–methoxy–4–alkoxybenzaldehydes were prepared by alkylation of vanillin[3].

Alkoxybenzylthioureas : These were prepared from alkoxybenzyl *iso*thiocyanates by the action of ammonia[1]. The thioureas were crystallised from alcohol and are described in Table II.

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TABLE 1

Alkoxybenzyl *iso*thiocyanates

R –$ArCH_2NCS$

No.	*R*	*B.P.°C*	*Mol. Formula*	*%Sulphur* Found	Calcd.
1.	4–*n*–propoxy	165–70/5 m.m.	$C_{11}H_{13}NOS$	15.4	15.4
2.	4–*n*–amyloxy	140–43/3 m.m.	$C_{13}H_{17}NOS$	13.4	13.6
3.	4–*n*–hexoxy	145–50/9 m.m.	$C_{14}H_{19}NOS$	12.7	12.8
4.	3,4–dimethoxy	140–45/9 m.m.	$C_{10}H_{11}NO_2S$	15.3	15.3
5.	4.–ethoxy–3–methoxy	167–70/9 m.m.	$C_{11}H_{13}NO_2S$	14.4	14.3
6.	4–*n*–propoxy–3–methoxy	145–50/5 m.m.	$C_{12}H_{15}NO_2S$	13.6	13.5
7.	4–*n*–butoxy–3–methoxy	175–80/5 m.m.	$C_{13}H_{17}NO_2S$	12.6	12.7
8.	4–*n*–amyloxy–3–methoxy	143–47/4 m.m.	$C_{14}H_{19}NO_2S$	12.0	12.1
9.	4–*n*–hexoxy–3–methoxy	185–91/4 m.m.	$C_{15}H_{21}NO_2S$	11.4	11.5

TABLE II

1–(Alkoxybenzyl)–2–thioureas

R—$ArCH_2NHCSNH_2$

No.	*R*	*M.P.°C*	*Mol. Formula*	*%Sulphur* Found	Calcd.
1.	4–*n*–propoxy	111	$C_{11}H_{16}N_2OS$	14.3	14.3
2.	4–*n*–amyloxy	113	$C_{13}H_{20}N_2OS$	12.6	12.7
3.	4–*n*–hexoxy	106	$C_{14}H_{22}N_2OS$	12.1	12.0
4.	3,4–dimethoxy	189	$C_{10}H_{14}N_2O_2S$	14.1	14.2
5.	4–ethoxy–3–methoxy	160	$C_{11}H_{16}N_2O_2S$	13.2	13.3
6.	4–*n*–propoxy–3–methoxy	172	$C_{12}H_{18}N_2O_2S$	12.5	12.6
7.	4–*n*–butoxy–3–methoxy	145	$C_{13}H_{20}N_2O_2S$	12.1	11.9
8.	4–*n*–amyloxy–3–methoxy	119	$C_{14}H_{22}N_2O_2S$	11.3	11.3
9.	4–*n*–hexoxy–3–methoxy	90	$C_{15}H_{24}N_2O_2S$	10.7	10.8

The authors thank Shri. Khambhat Taluka Sarvajanik Kelavani Mandal for facilities, Dr. P. S. Satpanthi for his interest and Department of Industries, Gujarat State for a fellowship to M. C. Shroff.

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THIAZOLIDONES PART XI

SYNTHESIS OF 2--ALKOXYBENZYLIMINO-4-THIAZOLIDONES AND THEIR BENZAL DERIVATIVES

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Summary

Alkoxybenzylthioureas are condensed with chloroacetic acid to give 2–alkoxybenzylimino–4–thiazolidones. These condense with aldehydes to give benzal derivatives.

In continuation of our earlier work, alkoxybenzyl and 3–methoxy–4-alkoxybenzylthioureas have been condensed with chloroacetic acid to give 2–(4–alkoxy/3-methoxy-4-alkoxybenzyl)-imino-4-thiazolidones. These smoothly condense with aldehydes in presence of sodium acetate to give benzal derivatives.

Experimental

All melting points are uncorrected.

The condensation of alkoxybenzylthioureas with chloroacetic acid to yield 4-thiazolidones and conversion of these into benzal derivatives was carried out as described earlier.[1] The required thioureas are described elsewhere.[2]

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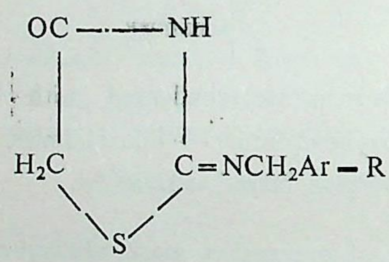
2–Alkoxybenzylimino–4–thiazolidones are described in Table I and the benzal derivatives are described in Table II.

The authors thank Shri Khambhat Taluka Sarvajanik Kelavani Mandal for facilities, Dr. P. S. Satpanthi for his interest and Department of Industries, Government of Gujarat for a fellowship to M. C. Shroff and Gujarat Pharmaceutical and Chemical Works : Ahmedabad, for gift of Chemicals.

TABLE I

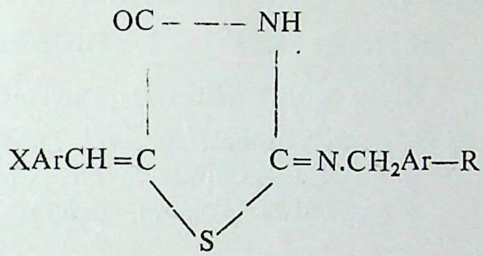
2–(Alkoxybenzyl)--imino-4-thiazolidones



No.	*R*	*M.P.°C*	*Mol. Formula*	*% Sulphur* Found	Calcd.
1.	4–ethoxy	176	$C_{12}H_{14}N_2O_2S$	12.7	12.8
2.	4–n–propoxy	141	$C_{13}H_{16}N_2O_2S$	11.9	12.1
3.	4–n–butoxy	151	$C_{14}H_{18}N_2O_2S$	11.5	11.5
4.	4–n–amyloxy	120	$C_{15}H_{20}N_2O_2S$	10.9	11.0
5.	4–n–hexoxy	148	$C_{16}H_{22}N_2O_2S$	10.4	10.5
6.	3,4–dimethoxy	178	$C_{12}H_{14}N_2O_3S$	11.9	12.0
7.	4–ethoxy–3–methoxy	137	$C_{13}H_{16}N_2O_3S$	11.4	11.4
8.	4–n–propoxy-3-methoxy	181	$C_{14}H_{18}N_2O_3S$	10.8	10.9
9.	4–n–butoxy–3–methoxy	135	$C_{15}H_{20}N_2O_3S$	10.4	10.4
10.	4–n–amyloxy–3–methoxy	132	$C_{16}H_{22}N_2O_3S$	9.8	9.9
11.	4–n–hexoxy–3–methoxy	130	$C_{17}H_{24}N_2O_3S$	9.5	9.5

TABLE II

2–(Alkoxybenzyl)–imino–5–benzylidene–4–thiazolidones



No.	R	X	M.P.°C	Molecular Formula	% Sulphur Found	% Sulphur Calcd.
1.	4–ethoxy	4–Cl	218	$C_{19}H_{17}ClN_2O_2S$	8.6	8.6
2.	4–n–propoxy	4–Cl	206	$C_{20}H_{19}ClN_2O_2S$	8.2	8.3
3.	4-n–butoxy	4–Cl	195	$C_{21}H_{21}ClN_2O_2S$	7.9	8.0
4.	4-n–amyloxy	4–Cl	181	$C_{22}H_{23}ClN_2O_2S$	7.5	7.7
5.	4-n–amyloxy	2,4-(Cl)$_2$	178	$C_{22}H_{22}Cl_2N_2O_2S$	7.0	7.1
6.	4–n–hexoxy	4–Cl	163	$C_{23}H_{25}ClN_2O_2S$	7.4	7.5
7.	3,4–dimethoxy	4–Cl	209	$C_{19}H_{17}ClN_2O_3S$	8.2	8.2
8.	4–ethoxy–3–methoxy	4–Cl	227	$C_{20}H_{19}ClN_2O_3S$	7.9	7.9
9.	4–n–propoxy–3–methoxy	4–Cl	201	$C_{21}H_{21}ClN_2O_3S$	7.9	7.7
10.	4–n–propoxy–3–methoxy	2,4-(Cl)$_2$	204	$C_{21}H_{20}Cl_2N_2O_3S$	7.2	7.1
11.	4–n–propoxy-3-methoxy	4–OCH$_3$	112	$C_{22}H_{24}N_2O_4S$	7.6	7.7
12.	4–n–butoxy-3-methoxy	4–Cl	194	$C_{22}H_{23}ClN_2O_3S$	7.3	7.4
13.	4-n–amyloxy-3-methoxy	4–Cl	182	$C_{23}H_{25}ClN_2O_3S$	7.0	7.2
14.	4–n–hexoxy–3-methoxy	4–Cl	154	$C_{24}H_{27}ClN_2O_3S$	6.9	7.0

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BENZYLTHIOUREAS PART V

SYNTHESIS OF 1--BENZYL--3--(2--METHYLPYRIDYL/3--METHYLPYRIDYL)--2--THIOUREAS

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Summary

The title compounds were prepared by condensing 2–/3–pyridylmethylamines with benzyl *iso*thiocyanates.

Benzyl *iso*thiocyanates and benzylthioureas have been shown to exhibit bacteriostatic and fungitoxic properties.[1]

1–Benzyl–3–(2–methylpyridyl/3–methylpyridyl)–2–thioureas have been prepared by condensation of benzyl *iso*thiocyanates with 2–/3–pyridylmethylamines in order to study the effect of heterocyclic ring on antimicrobial properties.

Experimental

All melting points are uncorrected.

The required benzyl *iso*thiocyanates were prepared as described earlier.[1a, b.]

1–Benzyl–3–(2–methylpyridyl/3–methylpyridyl)–2–thioureas :

A mixture of benzyl *iso*thiocyanates (0.01 mole) and 2--/3--pyridylmethylamine (0.01 mole) in absolute alcohol (25--40 ml.) was heated to boiling for a few minutes and kept overnight. The crystalline thioureas obtained were purified by recrystallisation from ethyl alcohol.

Compounds prepared are shown in Table.

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TABLE

1-Benzyl-3-(2-methylpyridyl/3-methylpyridyl)-2-thioureas

$X\text{-}ArCH_2NHCSNHCH_2\text{-}R$

No.	*X*	*R*	*M.P.°C*	*Mol. Formula*	*% Sulphur Found*	*Calcd.*
1.	H	2-pyridyl	116-17	$C_{14}H_{15}N_3S$	12.5	12.5
2.	2-Cl	2-pyridyl	117	$C_{14}H_{14}ClN_3S$	10.9	11.0
3.	3-Cl	2-pyridyl	121	$C_{14}H_{14}ClN_3S$	10.8	11.0
4.	4-Cl	2-pyridyl	120	$C_{14}H_{14}ClN_3S$	10.7	11.0
5.	$2\text{-}CH_3$	2-pyridyl	130	$C_{15}H_{17}N_3S$	11.7	11.8
6.	$3\text{-}CH_3$	2-pyridyl	86	$C_{15}H_{17}N_3S$	11.6	11.8
7.	$4\text{-}CH_3$	2-pyridyl	153.	$C_{15}H_{17}N_3S$	11.9	11.8
8.	$3,4\text{-}(CH_3)_2$	2-pyridyl	87-88	$C_{16}H_{19}N_3S$	11.1	11.2
9.	$2,4\text{-}(CH_3)_2$	2-pyridyl	130-31	$C_{16}H_{19}N_3S$	11.3	11.2
10.	$2,5\text{-}(CH_3)_2$	2-pyridyl	126	$C_{16}H_{19}N_3S$	11.1	11.2
11.	$4\text{-}0CH_3$	2-pyridyl	85	$C_{15}H_{17}N_3OS$	11.0	11.1
12.	H	3-pyridyl	128	$C_{14}H_{15}N_3S$	12.4	12.5
13.	2-Cl	3-pyridyl	132	$C_{14}H_{14}ClN_3S$	11.2	11.0
14.	3-Cl	3-pyridyl	141	$C_{14}H_{14}ClN_3S$	11.3	11.0
15.	4-Cl	3-pyridyl	136	$C_{14}H_{14}ClN_3S$	11.1	11.0
16.	$2\text{-}CH_3$	3-pyridyl	140	$C_{15}H_{17}N_3S$	11.9	11.8
17.	$3\text{-}CH_3$	3-pyridyl	78	$C_{15}H_{17}N_3S$	11.7	11.8
18.	$4\text{-}CH_3$	3-pyridyl	112	$C_{15}H_{17}N_3S$	11.9	11.8
19.	$3,4\text{-}(CH_3)_2$	3-pyridyl	86	$C_{16}H_{19}N_3S$	11.3	11.2
20.	$2,4\text{-}(CH_3)_2$	3-pyridyl	132	$C_{16}H_{19}N_3S$	11.1	11.2
21.	$2,5\text{-}(CH_3)_2$	3-pyridyl	141	$C_{16}H_{19}N_3S$	11.0	11.2
22.	$4\text{-}0CH_3$	3-pyridyl	80	$C_{15}H_{17}N_30S$	11.2	11.1

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SYNTHESIS OF SOME PYRAZOLINES AND ISO-OXAZOLINES DERIVED FROM 4-CHLORO AND 4-BROMO QUINACETO-PHENONE MONOMETHYL ETHERS

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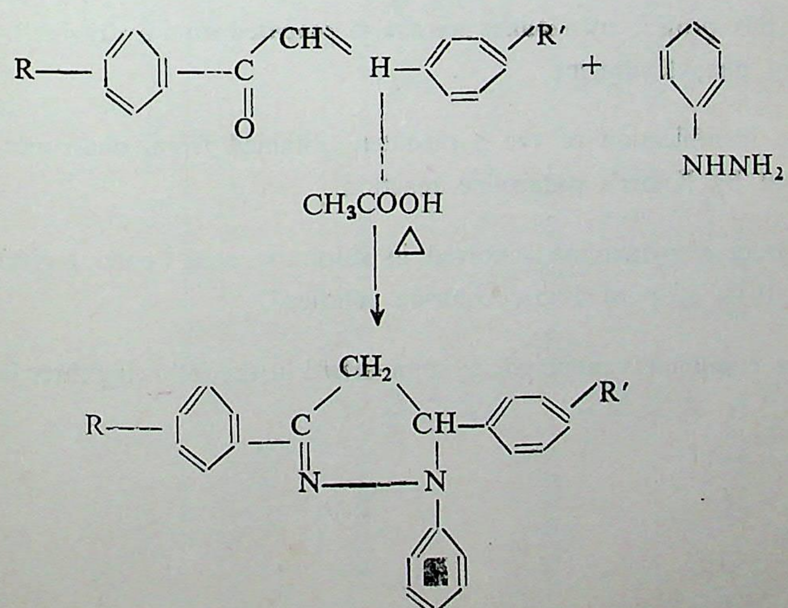
Some chalkones derived from 4-chloro and 4-bromo quinacetophenone monomethyl ethers have been converted into Pyrozolines by heating them with hydrazine as well as phenylhydrazine in glacial acetic acid. Iso-oxazoline derivatives were also prepared by refluxing a pyridine solution of the halogenated chalkones with Hydroxylamine hydrochloride.

* * *

As is well known, the presence of a carbonyl group (C=0) in an aromatic compound is detected by preparing its 2, 4,-Dinitrophenyl-hydrazone, which is usually a good crystalline derivative[1].



Sometimes, due to the labile nature of the hydrazone; ring closure takes place and isomeric pyrazolines are produced instead of the expected hydrazones. According to Raiford and Peterson[2] this depends upon the nature of the substituents in the ketone. They also found that the phenyl hydrazones can be also converted into pyrazolines by heating them with acetic acid.

The chalkones contain α-β-unsaturated grouping and react with phenylhydrazine and form pyrazolines. Similarly it is known that the chalkone dibromides on treatment with hydroxylamine hydrochloride yield the corresponding Iso-oxazolines.

Nadkarni, Warriar and Wheeler[3] stated that the same iso-oxazolines could be obtained by the action of hydroxylamine hydrochloride of the corresponding diketone. On the other hand, they found that the dibromide $PhCOCHBr.CHBr.C_6H_4OMe$ gave 3-phenyl-5-anisyl Iso-oxazole; whereas, the diketones $PhCOCH_2COC_6H_4OMe$ gave 5-phenyl-3-anisyl Iso-oxazole[4]. In continuation of the above work, Shenoi, Shah and Wheeler[5] have also carried out exhaustive work and have supported that 3-Iso-oxazole is the main product in most of the cases. Joshi and Jauhar[6] prepared Iso-oxazoline derivatives by refluxing a pyridine solution of the chalkone with hydroxylamine hydrochloride.

In this project pyrazolines were also prepared from hydrazine hydrate instead of phenylhydrazine.

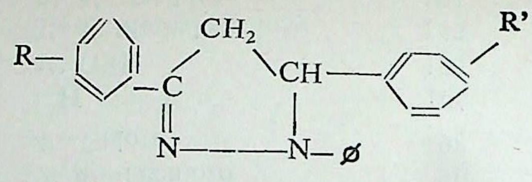
The identification of the pyrazolines obtained from chalkones was carried out by Knorr's pyrazoline reaction.

A trace of pyrazoline dissolved in sulphuric acid (conc.) gives blue colour with a drop of Ferric chloride solution[7].

The compounds prepared are summarised in the following three tables :

TABLE I

TABLE I

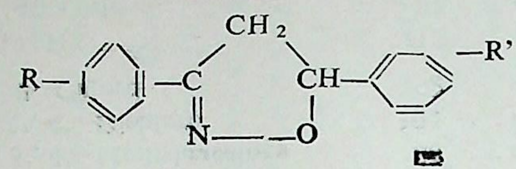


1 Phenyl—3, 5, (Substituted Phenyl)—Δ^2—Pyrazoline

R =	*R′* =	*M. P.*	*Molecular Formula*	*% N* Found	*% N* Reqd.
1	2	3	4	5	6
2″ Hydroxy–4″ –Chloro–5″ OMe	—H	100	$C_{22}H_{19}ClN_2O_2$	7.32	7.40
—Do—	4′—OMe	79	$C_{23}H_{21}ClN_2O_3$	6.81	6.86
—Do—	3′, 4′—Methylenedioxy	86	$C_{23}H_{19}ClN_2O_4$	6.57	6.63
—Do—	2′, 4′—Dichloro	105	$C_{22}H_{17}Cl_3N_2O_2$	6.22	6.26
—Do—	4′—Chloro	99	$C_{22}H_{18}Cl_2N_2O_2$	6.59	6.78
2″—Hydroxy—4″—Bromo—5″—OMe	—H	112	$C_{22}H_{19}BrN_2O_2$	6.48	6.62
—Do—	4′—OMe	92	$C_{23}H_{21}BrN_2O_3$	6.09	6.18
—Do—	3′,4′—Methylenedioxy	97	$C_{23}H_{19}BrN_2O_4$	5.89	6.00
—Do—	2′,4′—Dichloro	115	$C_{22}H_{17}BrCl_2N_2O_2$	5.56	5.69
—Do—	4′—Chloro	124	$C_{22}H_{18}BrClN_2O_2$	5.74	5.86
2″, 5″—DI—OMe—4″—Chloro	—H	92	$C_{23}H_{21}ClN_2O_2$	7.07	7.13
—Do—	4′—OMe	96	$C_{24}H_{23}ClN_2O_3$	6.55	6.63
—Do—	3′, 4′—Methylenedioxy	62	$C_{24}H_{21}ClN_2O_4$	6.33	6.41
—Do—	2′, 4′—Dichloro	78	$C_{23}H_{19}Cl_3N_2O_2$	5.93	6.07
—Do—	4′—Chloro	105	$C_{23}H_{20}Cl_2N_2O_2$	6.47	6.56

1	2	3	4	5	6
2″, 5″—DI—OMe—4″—Bromo	—H	100	$C_{23}H_{21}BrN_2O_2$	6.35	6.41
—Do—	4′—OMe	95	$C_{24}H_{23}BrN_2O_3$	5.78	6.00
—Do—	3′,4′—Methylenedioxy	82	$C_{24}H_{21}BrN_2O_4$	5.67	5.82
—Do—	2′, 4′—Dichloro	121	$C_{23}H_{19}BrCl_2N_2O_2$	5.36	5.50
—Do—	4′—Chloro	120	$C_{23}H_{20}BrClN_2O_2$	5.87	5.94

TABLE II

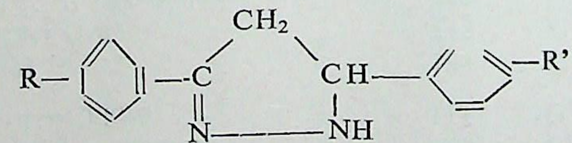


3, 5, (Substituted Phenyl)—$\triangle^2$—Iso—Oxazolines

R=	*R′* =	*M. P.*	*Molecular Formula*	*% N Found*	*% N Reqd.*
2″—Hydroxy—4″—Chloro—5″—OMe	—H	87	$C_{16}H_{14}ClNO_3$	4.53	4.61
—Do—	4′—OMe	105	$C_{17}H_{16}ClNO_4$	4.09	4.20
—Do—	3′, 4′—Methylenedioxy	109	$C_{17}H_{14}ClNO_5$	3.90	4.03
—Do—	2′, 4′—Dichloro	90	$C_{16}H_{12}Cl_3NO_3$	3.63	3.76
—Do—	4′—Chloro	98	$C_{16}H_{13}Cl_2NO_3$	4.04	4.14
2″—Hydroxy—4″—Bromo—5″—OMe	—H	108	$C_{16}H_{14}BrNO_3$	3.87	4.02
—Do—	4′—OMe	137	$C_{17}H_{16}BrNO_4$	3.48	3.69
—Do—	3′, 4′ Methylenedioxy	143	$C_{17}H_{14}BrNO_5$	3.50	3.57
—Do—	2′, 4′—Dichloro	101	$C_{16}H_{12}BrCl_2NO_3$	3.27	3.35
—Do—	4′—Chloro	85	[illegible]	3.54	3.66

2″, 5″—DI—OMe—4″—Chloro	—H	105	$C_{17}H_{16}ClNO_3$	4.31	4.41
—Do—	4′—OMe	76	$C_{18}H_{18}ClNO_4$	3.89	4.03
—Do—	3′, 4′ Methyenedioxy	128	$C_{18}H_{16}ClNO_5$	3.62	3.87
—Do—	2′, 4′—Dichloro	105	$C_{17}H_{14}Cl_3NO_3$	3.47	3.62
—Do—	4′—Chloro	74	$C_{17}H_{15}Cl_2NO_3$	3.73	3.98
2″, 5″—DI—OMe—4″—Bromo	H	144	$C_{17}H_{16}BrNO_3$	3.74	3.87
—Do—	4′—OMe	96	$C_{18}H_{18}BrNO_5$	3.39	3.57
—Do—	3′, 4′ Methylenedioxy	70	$C_{18}H_{16}BrNO_5$	3.28	3.45
—Do—	2′, 4′—Dichloro	114	$C_{17}H_{14}BrCl_2NO_3$	3.13	3.25
—Do—	4′—Chloro	110	$C_{17}H_{15}BrClNO_3$	3.44	3.53

TABLE III



3, 5—(Substituted Phenyt)—Δ^2—Pyrazolines

R=	*R′=*	*M. P.*	*Molecular Formula*	*% N Found*	*% N Reqd.*
1	2	3	4	5	6
2″—Hydroxy—4″—Chloro—5″—OMe	—H	120	$C_{16}H_{15}ClN_2O_2$	9.24	9.27
—Do—	4′—OMe	145	$C_{17}H_{17}ClN_2O_3$	8.37	8.42
—Do—	3′—4′—Methylenedioxy	140	$C_{17}H_{15}ClN_2O_4$	7.95	8.08
—Do—	2′, 4′—Dichloro	100	$C_{16}H_{13}Cl_3N_2O_2$	7.47	7.54
—Do—	4″—Chloro	104	$C_{16}H_{14}Cl_2N_2O_2$	8.23	8,31

1	2	3	4	5	6
2″—Hydroxy—4″—Bromo—5″—OMe	H	125	$C_{16}H_{15}BrN_2O_2$	7.95	8.07
—Do—	4′—OMe	171	$C_{17}H_{17}ClN_2O_3$	7.28	7.43
—Do—	3′, 4′—Methylenedioxy	144	$C_{17}H_{15}ClN_2O_4$	7.01	7.16
—Do—	2′, 4′—Dichloro	165	$C_{16}H_{13}Cl_2N_2O_2$	6.59	6.73
—Do—	4′—Chloro	108	$C_{16}H_{14}BrClN_2O_2$	7.27	7.34
2″, 5″—DI—OMe—4″—Chloro	H	110	$C_{17}H_{17}ClN_2O_2$	8.81	8.85
—Do—	4′—OMe	108	$C_{18}H_{19}ClN_2O_3$	7,90	8.08
—Do—	3′, 4′—Methylenedioxy	130	$C_{18}H_{17}ClN_2O_4$	7.69	7.78
—Do—	2′, 4′—Dichloro	120	$C_{17}H_{15}Cl_3N_2O_2$	7.12	7.26
—Do—	4′—Chloro	115	$C_{17}H_{16}Cl_2N_2O_2$	7.85	7.98
2″, 5″—DI—Ome—4″—Bromo	H	145	$C_{17}H_{17}BrN_2O_2$	7.72	7.76
—Do—	4′—OMe	115	$C_{18}H_{19}BrN_2O_3$	7.02	7.16
—Do—	3′, 4′—Methylenedioxy	150	$C_{18}H_{17}BrN_2O_4$	6.82	6.91
—Do—	2′, 4′—Dichloro	113	$C_{17}H_{15}BrCl_2N_2O_2$	6.42	6.51
—Do—	4′—Chloro	128	$C_{17}H_{16}Br\ \ IN_2O_2$	6.95	7.08

Experimental

Pyrazolines : The required chalkone (1 Mole) was added to phenylhydrazine/hydrazine hydrate (1.1 Mole) in glacial acetic acid[8] and the reaction mixture was refluxed for three hours. It was then diluted with cold water and solid which separated was then crystallised from ethanol. (In addition to Knorr's pyrazoline reaction they were exposed to bromine vapours with which they gave green colour[9].)

Iso-oxazolines : To a solution of hydroxylamine hydrochloride (1.2 Mole) in water were added the required amount of halogenated chalkone (1 Mole) and pyridine[10]. Reaction mixture was then refluxed for four hours. It was then acidified with dilute acetic acid and if necessary kept. over night. The product was then crystalised from benzene or petrolether.

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ON REPRESENTING AN INTEGER AS A SUM OF TWO TRIANGULAR NUMBERS

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For $k \geqslant 1$, the k th triangular number is $T_k = \frac{1}{2}k(k+1)$. Sierpinski [1] has shown that the triangular number T_n is a sum of two triangular numbers if and only if $n^2+(n+1)^2$ is a composite integer. In this note we extend Sierpinski's result to an arbitrary integer. We prove

Theorem : A positive integer k can be expressed as a sum of two triangular numbers if and only if $4k+1$ can be expressed in the form

$$u^2+v^2 \text{ with } u-v \geqslant 3.$$

Suppose $k = T_a + T_b$, $a \geqslant 1$, $b \geqslant 1$, then

$$\begin{aligned} 4k+1 &= 2a(a+1)+2b(b+1)+1 \\ &= 2(a^2+b^2)+2(a+b)+1 \\ &= (a+b+1)^2+(a-b)^2. \end{aligned}$$

Putting $u=a+b+1$, $v=a-b$, we find that

$$4k+1 = u^2+v^2 \text{ with } u-v = 2b+1 \geqslant 3.$$

Conversely, suppose $4k+1 = u^2+v^2$ with $u-v \geqslant 3$. Then obviously u and v are of opposite parity and

$$4k+1 = \tfrac{1}{2}\left\{(u+v-1)(u+v+1)+(u-v-1)(u-v+1)\right\}+1,$$

i.e. $k = \frac{1}{2}\left\{\frac{1}{2}(u+v-1)\cdot\frac{1}{2}(u+v+1)\right\}$
$+\frac{1}{2}\left\{\frac{1}{2}(u-v-1)\cdot\frac{1}{2}(u-v+1)\right\}$,

i.e. $k = T_a + T_b$, where $a = \frac{1}{2}(u+v-1)$, $b = \frac{1}{2}(u-v-1)$ and we note that $a \geqslant 1$, $b \geqslant 1$.

In the rest of this note, we show that Sierpinski's result can be derived from the above theorem.

If $k = T_n = \frac{1}{2}n(n+1)$, then $4k+1 = 2n(n+1)+1 = n^2+(n+1)^2$. Sierpinski's result would therefore follow from our theorem with the help of the following

Lemma : Let n be a positive integer. The integer $n^2+(n+1)^2$ can be expressed in the form u^2+v^2 with $u-v \geqslant 3$ if and only if it is composite.

Proof : If $n^2+(n+1)^2$ is a prime, then it is a prime$\equiv 1 \pmod 4$ and as is well known, such primes can be expressed in essentially only one way as a sum of two squares and we already have that unique representation as $n^2+(n+1)^2$ and this representation does not satisfy the condition $u-v \geqslant 3$.

Next suppose $n^2+(n+t)^2 = t$ is composite. Let $t = gh$, where g is not divisible by any prime$\equiv 3 \pmod 4$ and h is not divisible by any prime$\equiv 1 \pmod 4$. If $r(t)$ is the total number of representations of t as a sum of two squares (positive, negative or zero, the order in which the squares are written also being important), then it is known that $r(t) = 0$ or $r(t) = 4d(g)$ according as h is not or is a perfect square. Now, since $t = n^2+(n+1)^2$, we know that $r(t) \geqslant 8$ and therefore h must be a square, $h = m^2$. If g is not a prime, then $d(g) \geqslant 3$, so that $r(t) = 4d(g) \geqslant 12$, implying that $t = u^2+v^2$ with $u^2 \neq n^2$, $v^2 \neq n^2$, and hence $u-v \geqslant 3$. If g is a prime, then $t = gm^2$ implies that $m^2 > 1$, i.e. $m \geqslant 3$. Also as $t \equiv 1 \pmod 4$, g is a prime$\equiv 1 \pmod 4$, so that $g = y^2+z^2$ with $y-z \geqslant 1$.

Therefore $t = gm^2 = (y^2+z^2)m^2 = (my)^2+(mz)^2$ with $my-mz = m(y-z) \geqslant 3$. This completes the proof of the lemma.

Reference

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EXPLICIT FORMULAS FOR $\sum_{i=1}^{n} i^r (\equiv S_r)$ AND BERNOUILLI'S NUMBERS B_r

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1. Introduction :

Bernard and Child[1] have obtained recurrence relations containing S_{2r-1}, S_{2r-3}......S_3, S_1, and also S_{2r}, S_{2r-2}......S_4, S_2. They[2] have also written recurrence relations containing B_r, B_{r-1}......B_1, A formula for S_r in terms of B_r's have been stated in their Book[3]. Smith[4] has discussed a method to obtain explicitely S_4, S_6, S_8 etc. It is difficult to obtain S_r for larger values of r, by their method.

In this paper, formulas for S_{2r-1}, S_{2r}, S_r and B_r have been obtained explicitely by using matrices and their inverses. Certain relations between matrices are also obtained.

2. Formula for S_{2r-1}.

2-*a*. Notations :

(*i*) C_s^r = 5th Binomial coefficient in the expansion of

$$(1+x)^r \text{ when } s \leq r$$
$$= 0 \qquad s > r. \qquad \ldots (1)$$

(*ii*) Matrix $(A) = \begin{vmatrix} C_1^r & C_3^r & \ldots & \ldots & C_{2r-1}^r \\ 0 & C_1^{r-1} & \ldots & \ldots & C_{2r-3}^{r-1} \\ 0 & 0 & C_1^{r-1} & \ldots & C_{2r-5}^{r-2} \\ 0 & 0 & \ldots & 0 & C_1^r \end{vmatrix}$, $|A|$ = Determinant of the matrix (A) $\qquad \ldots (2)$

(*iii*) $|A_0^r| = 1, \quad |A_1^r| = C_3^r, \quad |A_2^r| = \begin{vmatrix} C_3^r & C_5^r \\ C_1^{r-1} & C_3^{r-1} \end{vmatrix}$ ... (3)

$$|A_3^r| = \begin{vmatrix} C_3^r & C_5^r & C_7^r \\ C_1^{r-1} & C_3^{r-1} & C_5^{r-1} \\ 0 & C_1^{r-2} & C_3^{r-2} \end{vmatrix} \quad \text{... (4)}$$

$$|A_s^r| = \begin{vmatrix} C_3^r & C_5^r & \dots & C_{2s+1}^r \\ C_1^{r-1} & C_3^{r-1} & \dots & C_{2s-1}^{r-1} \\ 0 & & & \\ 0 & & & \\ 0 & \dots & \dots & C_3^{r-s} \end{vmatrix} \quad \text{... (5)}$$

(*iv*) The inverse of matrix $(A) = A^{-1}$

$$= \begin{pmatrix} a_{11} & a_{12} & \dots & a_{1r} \\ a_{21} & a_{22} & \dots & a_{2r} \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ a_{s1} & a_{s2} & \dots & a_{sr} \\ \dots & \dots & \dots & \dots \\ a_{r1} & a_{r2} & \dots & a_{rr} \end{pmatrix} \quad \text{... (6)}$$

Where

$$a_{11} = \frac{|A_0^r|}{r}, \; a_{12} = \frac{(-1)|A_1^r|}{r(r-1)}, \; a_{13} = \frac{(-1)^2|A_2^r|}{r(r-1)(r-2)}, \quad \text{... (7)}$$

$$a_{1r} = \frac{(-1)^{r-1}|A_{r-1}|}{r(r-1)\dots\dots 1}$$

1-b. Method :

Bernard and Child have given the following formula :

$$C_1^r \; S_{2r-1} + C_3^r \; S_{2r-3} + C_5^r \; S_{2r-5} \; \dots = \frac{\sigma^r}{2} \quad \text{... (8i)}$$

Taking $r-1$, $r-2$......1 successively in place of r

$$C_1^{r-1} \; S_{2r-3} + C_3^{r-1} \; S_{2r-5} \; \dots = \frac{\sigma^{r-1}}{2} \quad \text{... (8ii)}$$

$$C_1^{r-1}\ S_{2r-5}+C_3^{r-2}\ S_{2r-7}\ \cdots = \frac{\sigma^{r-2}}{2} \quad \cdots \quad (8iii)$$

$$\cdots \qquad \cdots \qquad \cdots \qquad \cdots$$

$$\cdots \qquad \cdots \qquad \cdots \qquad \cdots$$

$$C_1^{2}\ S_3\ \cdots = \frac{\sigma^{2}}{2} \quad \cdots \quad (8_{(s-1)})$$

$$C_1^{1}\ S_1\ \cdots = \frac{\sigma}{2} \quad \cdots \quad (8_r)$$

Where $\sigma = n\ (n+1)$

let the row vector $S=[S_{2r-1}, S_{2r-3} \ldots S_3, S_1]$ ... (9)

and the column vector $[\sigma^1] = \begin{bmatrix} \frac{\sigma^r}{2} \\ \frac{\sigma^{r-1}}{2} \\ \cdots \\ \frac{\sigma}{2} \end{bmatrix}$ ... (10)

The matrix equation of the above equations is

$$(A)\,(S)=(\sigma) \quad \ldots \quad (11)$$

From (11), we get

$$(S)=(A)^{-1}\,(\sigma) \quad \ldots \quad (12)$$

Hence

$$S_{2r-1}=a_{11}\frac{\sigma^r}{2}+a_{12}\frac{\sigma^{r-1}}{2}\ \cdots\ \cdots\ \cdots+a_{1r}\frac{\sigma}{2} \quad \ldots \quad (13)$$

We deduce

$$S_{2r-1}=\frac{|A_0^r|}{r}\frac{\sigma^r}{2}+\frac{(-1)\,|A_1^r|}{r(r-1)}\frac{\sigma^{r-1}}{2}+\frac{(-1)^2\,|A_2^r|}{r(r-1)(r-2)}\frac{\sigma^{r-2}}{2}\ \cdots$$

$$\cdots+\frac{(-1)^{r-1}\,|A^r_{r-1}|}{r(r-1)\ldots\ldots 1}\frac{\sigma}{2} \quad \ldots \quad (14)$$

2–c. Calculations :

$A_0^1=A_0^2=A_0^3\ldots\ldots=1$ ... (15)

$A_1^1=A_1^2=0,\ A_1^3=1,\ A_1^4=4,\ A_1^5=10,\ A_1^6=20$ ... (16)

$A_2^1=A^2_2=A^3_2=0,\ A_2^4=4,\ A_2^5=36,\ A_2^6=170$ ... (17)

$A_3^1=A_3^2=A_3^3=A_3^4=0,\ A_3^5=40,\ A_3^6=110,$ ... (18)

Putting $r=1$ in (14) and using the above results

$$S_1 = \frac{\sigma}{2} \qquad \dots (19)$$

Putting $r=2$ in (14) and using the above results

$$S_3 = \frac{\sigma^2}{4} \qquad \dots (20)$$

For $r=3$, we get

$$S_5 = \frac{\sigma^3}{6} - \frac{\sigma^2}{12} = \frac{\sigma^2}{12}(2\sigma - 1) \qquad \dots (21)$$

In the same way

$$S_7 = \frac{\sigma^4}{8} - \frac{\sigma^3}{6} + \frac{\sigma^2}{12}$$

$$= \frac{\sigma^2}{24}[\sigma^2 - 4\sigma + 2] \qquad \dots (22)$$

All these results agree with results obtained by Bernard and Child.

3. Formula for S_{2r}

3-*a*. Notations :

$$\text{Matrix } (E) = \begin{pmatrix} 2r+1 & \frac{2r-1}{3} C_2^r & \frac{2r-3}{5} C_4^r & \cdots & \frac{3}{2r-1} C_{2r-2}^r \\ 0 & 2r-1 & \frac{2r-3}{3} C_2^{r-1} & \cdots & \frac{3}{2r-3} C_{2r-4}^{r-1} \\ 0 & 0 & 2r-3 & \cdots & \frac{3}{2r-5} C_{2r-6}^{r-2} \\ 0 & 0 & & 5 & \frac{3}{3} C_2^2 \\ 0 & \cdots\ 0 & & 0 & 3 \end{pmatrix} \quad \text{The determinant of matrix} = |E| \qquad \dots (23)$$

$$|E_0^r| = 1, \; |E_1^r| = \frac{2r-1}{3} C_2^r, \; |E_2^r| = \begin{vmatrix} \frac{2r-1}{3} C_2^r & \frac{2r-3}{5} C_4^r \\ 2r-1 & \frac{2r-3}{3} C_2^{r-1} \end{vmatrix} \qquad \dots (24)$$

$$| E_3^r | = \begin{vmatrix} \frac{2r-1}{3} C_2^r & \frac{2r-3}{5} C_4^r & \frac{2r-5}{7} C_6^r \\ (2r-1) & \frac{2r-3}{3} C_2^{r-1} & \frac{2r-5}{5} C_4^{r-1} \\ 0 & 2r-3 & \frac{2r-5}{3} C_2^{r-1} \end{vmatrix} \quad \dots (25)$$

$$| E_s^r | = \begin{vmatrix} \frac{2r-1}{3} C_2^r & \frac{2r-3}{5} C_4^r & \frac{2r-5}{7} C_6^r & \dots & \frac{2r-2s+1}{2s+1} C_{2s}^r \\ 2r-1 & \frac{2r-3}{3} C_2^{r-1} & \dots & \dots & \frac{2r-2s+1}{2s-1} C_{2r-2}^{r-1} \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \dots & \frac{2r-2s+1}{3} C_2^{r-s+1} \end{vmatrix} \dots (26)$$

(*iii*) The inverse of matrix $(E) = E^{-1}$.

$$= \begin{pmatrix} e_{11} & e_{12} & e_{13} & \dots & e_{1r} \\ e_{21} & e_{22} & \dots & \dots & e_{2r} \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ e_{r1} & e_{r2} & \dots & \dots & e_{rr} \end{pmatrix} \quad \dots (27$$

Where $e_{11} = \frac{|E^s{}_0|}{2r+1}$, $e_{12} = \frac{(-1)|E_1{}^r|}{(2r+1)(2r-1)}$, $e_{13} = \frac{(-1)^2 |E_2{}^r|}{(2r+1)(2r-1)(2r-3)}$

$$e_{1r} = \frac{(-1)^{r-1} |E^r{}_{r-1}|}{(2r+1)(2r-1)\dots 1} \quad \dots (28)$$

3·6. Method :

In Bernard and Child's formula, putting r, $r-1$, $r-2 \dots 1$ in place of r we get the following equations :

$$(2r+1)S_{2r} + \frac{2r-1}{3} C_2{}^r S_{2r-2} + \frac{2r-3}{5} C_4{}^r S_{2r-4} \dots = \frac{\sigma^r \sigma^1}{2} \quad \dots (29i)$$

$$(2r-1) S_{2r-2} + \frac{2r-3}{3} C^r{}_2 S_{2r-4} \dots \dots = \frac{\sigma^{r-1}\sigma^1}{2} \quad \dots (29ii)$$

$$(2r-3)S_{2r-4} + \frac{2r-5}{3} C_4{}^r S_{2r-6} + \dots \dots = \frac{\sigma^{r-2}\sigma^1}{2} \quad \dots (29iii)$$

$$5S_4+S_2=\frac{\sigma^2\sigma^1}{2} \qquad \text{... } (29_{r-1})$$

$$3S_2=\frac{\sigma\sigma^1}{2} \qquad \text{... } (29_r)$$

Let row vector $S^1=[2r,\ 2r-2\text{... ... ...}2]$ ... (30)

and column vector $\sigma^1=\begin{bmatrix}\frac{\sigma^r}{2}\sigma^1\\ \frac{\sigma^{r-1}}{2}\sigma^1\\ \cdots\\ \frac{\sigma\sigma^1}{2}\end{bmatrix}$ ... (31)

The matrix equation for the above equation is

$$(E)(S^1)=(\sigma^1) \qquad \text{... } (32)$$

$$(S)^1=(E^1)^{-1}(\sigma)^1 \qquad \text{... } (33)$$

So

$$S_{2r}=e_{11}\frac{\sigma^r\sigma^1}{2}+e_{12}\frac{\sigma^{r-1}\sigma^1}{2}+e_{13}\frac{\sigma^{r-1}\sigma^1}{2}\text{......}+e_{1r}\frac{\sigma\sigma^1}{2} \qquad \text{... } (34)$$

Hence

$$S_{2r}=\frac{|E_0{}^r|}{2r+1}\frac{\sigma^r\sigma^1}{2}+\frac{(-1)|E^r{}_1|}{(2r+1)(2r-1)}\frac{\sigma^{r-1}\sigma^1}{2}+\frac{(-1)^2|E^r{}_2|\sigma^{r-2}\sigma^1}{(2r+1)(2r-1)(2r-3)}$$

$$+\text{......}+\frac{(-1)^{r-1}|E^r{}_{r-1}|\sigma\sigma^1/2}{(2r+1)(2r-1)\text{...}1} \qquad \text{... } (35)$$

This is the explicit formula for S_{2r}.

3-c. Calculations :

$|E_0{}^1|=|E_0{}^2|=|E_0{}^3|= \quad =1$ ... (36)

$|E_1{}^1|=0,\ |E_1{}^2|=1,\ |E_1{}^3|=5,\ |E_1{}^4|=14,\ |E_1{}^5|=30$ ... (37)

$|E_2{}^1|=0, |E_2{}^2|=0,\ |E_2{}^3|=5,\ |E_2{}^4|=63;\ |E_2{}^5|=357$... (38)

$|E_3{}^1|=|E_3{}^2|=|E_3{}^3|=0\ \ |E_3{}^4|=63$ ... (39)

$|E_3{}^5|=1575$ ... (40)

Putting $r=1,\ 2,\ 3$......in succession in formula (35) and putting values of different E's

we get

$$S_2=\frac{\sigma\sigma^1}{6} \quad \text{... (41)}$$

$$S_4=\frac{\sigma^2\sigma^1}{10}-\frac{\sigma\sigma^1}{30}=\frac{\sigma\sigma^1}{30}\ (3\sigma-1) \quad \text{... (42)}$$

$$S_6=\frac{\sigma^3\sigma^1}{14}-\frac{\sigma^2\sigma^1}{14}+\frac{\sigma\sigma^1}{42}$$

$$=\frac{\sigma\sigma^1}{42}\ (3\sigma^2-3\sigma+1) \quad \text{... (43)}$$

These results agree with the results already obtained by Bernard and Child.

4. Formula for S_r

4-*a*. (*i*) Matrix $(D)=\begin{bmatrix} C_1^{r+1} & C_2^{r+1} & C_3^{r+1} & \dots & C_r^{r+1} \\ 0 & C_1^r & C_2^r & \dots & C_{r-1}^r \\ 0 & 0 & C_1^{r-1} & \dots & C_{r-2}^{r-1} \\ 0 & 0 & \dots & \dots & C_1^2 \end{bmatrix}$ The determinant of the matrix $=|D|$ ... (44)

$$|D_0^r|=1,\quad |D_1^r|=C_2^{r+1},\quad |D_2^r|=\begin{vmatrix} C_2^{r+1} & C_3^{r+1} \\ C_1^r & C_2^r \end{vmatrix} \quad \text{... (45)}$$

$$|D_3^r|=\begin{vmatrix} C_2^{r+1} & C_3^{r+1} & C_4^{r+1} \\ C_1^r & C_2^r & C_3^r \\ 0 & C_1^{r-1} & C_2^{r-1} \end{vmatrix} \quad \text{... (46)}$$

$$|D_s^r| = \begin{vmatrix} C_2^{r+1} & C_3^{r+1} & \dots & C_{s+1}^{r+1} \\ C_1^r & C_2^r & \dots & C_s^r \\ \dots & \dots & \dots & \dots \\ & & & C_2^{r-s+2} \end{vmatrix} \qquad \dots (47)$$

(*iv*) Inverse of Matrix $(D) = D^{-1}$.

$$= \begin{bmatrix} d_{11} & d_{12} & d_{13} & \dots & d_{1r} \\ d_{21} & d_{22} & d_{23} & \dots & d_{2r} \\ & & & & \\ d_{r1} & d_{r2} & & & d_{rr} \end{bmatrix} \qquad \dots (48)$$

Where

$$d_{11} = \frac{|D_0{}^r|}{r+1},\ d_{12} = \frac{(-1)\,|D_1{}^r|}{(r+1)\,r},\ d_{13} = \frac{(-1)^2\,|D_2{}^2|}{(r+1)\,r\,(r-1)}$$

$$d_{1r} = \frac{(-1)^{r-1}\,|D_{r-1}{}^r|}{(r+1)\,r\dots\dots2} \qquad \dots (49)$$

-b. Method:

Bernard and Child have given the following formula:

$$C_1{}^{r+1}S_r + C_1{}^{r+1}S_{r-1} + \dots + C_r{}^{r+1}S_1 = (n+1)^{r+1} - (n+1) \qquad \dots (50)$$

$$+ C_1{}^rS_{r-1} + \dots + C^r{}_{r-1}S_1 = (n+1)^r - (n+1) \qquad \dots (50i)$$

$$+ C_1{}^{r-1}S_{r-2}\dots \dots + C_{r-2}^{r-1}S_1 = (n+1)^{r-1} - (n+1) \qquad \dots (50ii)$$

$$\dots \qquad \dots \qquad \dots \qquad \dots$$

$$C_1{}^3S_2 + C_1{}^2S_1 = (n+1)^3 - (n+1) \qquad \dots (50_{r-1})$$

$$C_1{}^2S_1 = (n+1)^2 - (n+1) \qquad \dots (50_r)$$

Let the row vector $S^{11} = (S_r,\ S_{r-1}\dots S_2,\ S_1)$ ... (51)

and the column vector

$$N_r = \begin{bmatrix} (n+1)^{r+1} - (n+1) \\ (n+1)^r - (n+1) \\ \dots \\ \dots \\ (n+1)^2 - (n+1) \end{bmatrix} \qquad \dots (52)$$

The matrix equation for the above equations will be

$$(D)\ (S^{11}) = (N_r) \qquad \dots (53)$$

$$(S^{11}) = (D)^{-1}(N_r) \qquad \dots (54)$$

We get from it

$$S_r = \frac{|D_0^r|\ N_r}{r+1} - \frac{|D_1^r|\ N_{r-1}}{(r+1)\,r} + \frac{(-1)^2\ |D_2^r|\ N_{r-2}}{(r+1)\,r\,(r-1)} + \dots + \frac{(-1)^{r-1}N_1}{(r+1)\ r\dots 2}\dots \qquad \dots (55)$$

This is explicit formula for (S_r).

4-c. Calculations :

$$|D_0^1| = |D_0^2| = |D_0^3| = \dots\dots = 1 \qquad \dots (56)$$

$$|D_1^1| = 1,\ |D_1^2| = 3,\ |D_1^3| = 6,\ |D_1^4| = 10 \qquad \dots (57)$$

$$|D_2^1| = 0,\ |D_2^2| = 1,\ |D_2^3| = 6,\ |D_2^4| = 20 \qquad \dots (58)$$

$$|D_3^1| = |D_3^2| = 0,\ |D_3^3| = |D_3^4| = 0. \qquad \dots (59)$$

Putting 1, 2, 3,......in formula ( ) and putting values of D's

$$S_1 = \frac{N_1}{2} = \frac{n(n+1)}{2} \qquad \dots (60)$$

$$S_2 = \frac{N_2}{3} - \frac{N_1}{6} = \frac{n(n+1)(2n+1)}{6} \qquad \dots (61)$$

$$S_3 = \frac{N_3}{4} - \frac{6N_2}{4\cdot 3} + \frac{6N_1}{4\cdot 3\cdot 2}$$

$$= \frac{n(n+1)(n^2+3n+3)}{4} - \frac{n(n+1)((n+2)}{2} + \frac{n(n+1)}{4}$$

$$= \frac{n(n+1)}{4}\ (n^2+3n+3-2n-4+1)$$

$$= \frac{n^2(n+1)^2}{4} \qquad \dots (62)$$

The results agree with those obtained previously by Bernard and Child.

5. **Formula** for B_r and B_{2r}

From the reccurrence relation

$$C_1^{r+1}B_r + C_1^{r+1}B_{r-1}\ldots\ldots + C_r^{r+1}B_1 = r \qquad \ldots (66)$$

We get the matrix equation

$$(D)\,(B) = [R] \qquad \ldots (67)$$

Where

$$[B] = [B_r, B_{r-1}\ldots\ldots\ldots B_1] \qquad \ldots (68)$$

and

$$[R] = \begin{bmatrix} r \\ r-1 \\ r-2 \\ \vdots \\ 2 \\ 1 \end{bmatrix} \qquad \ldots (69)$$

$$(B) = (D)^{-1}(R)$$

So

$$B_r = \frac{|D_0{}^r|\,r}{r+1} - \frac{|D_1{}^r|\,(r-1)}{(r+1)(r)} + \frac{|D_2{}^r|\,(r-2)}{(r+1)r(r-1)}$$

$$+ \frac{(-1)^{r-1}\,|D_{r-1}{}^r|\,1}{(r+1)r(r-1)\ldots3\cdot2} \qquad \ldots (70)$$

So

$$B_1 = \frac{|D_0{}^1|}{2} = \tfrac{1}{2}$$

$$B_2 = \frac{|D_0{}^2|\,2}{3} - \frac{|D_1{}^2|}{3\cdot2}$$

$$= \frac{2}{3} - \frac{1}{2}$$

$$= \frac{1}{6} \qquad \ldots (71)$$

$$B_4 = \frac{|D_0{}^4|\,4}{5} - \frac{|D_1{}^4|\,3}{5\cdot4} + \frac{|D_2{}^4|\,2}{5\cdot4\cdot3} - \frac{|D_3{}^4|\,1}{5\cdot4\cdot3\cdot2}$$

$$= \frac{4}{5} - \frac{3}{2} + \frac{2}{3}$$

$$= \frac{24-45+20}{30}$$

$$= -\frac{1}{30}$$

The values of B_1, B_2, B_4 agree with those obtained by Bernard and Child.

5–b. Explicit formula for B_{2r} can be obtained from

$$(2r+1)\, B_{2r}+\tfrac{1}{8}\, C_2^r\,(2r-1)\, B_{2r-2}+\ldots=0,\; r\neq 1 \qquad \ldots (74)$$

for $r=1$ right of the above equation is $\frac{1}{2}$.

Hence Matrix relation is

$$E\cdot B^1=R^1 \qquad \ldots (75)$$

Where

$$B^1=[B_{2r},\; B_{2r-2}\ldots\ldots B_2] \qquad \ldots (76)$$

$$R^1=\begin{bmatrix} 0\\ 0\\ 0\\ \vdots\\ \frac{1}{2} \end{bmatrix} \qquad \ldots (77)$$

$$B^1=E^{-1}\; R^1$$

$$B_{2r}=\frac{(-1)^{r-1}\;\frac{1}{2}\,|E_{r-1}{}^r|}{(2r+1)(2r-1)\ldots 1} \qquad \ldots (78)$$

We have

$$E_0{}^1=1,\; E_1{}^2=1,\; E_2{}^3=5,\; E_3{}^4=63 \qquad \ldots (79)$$

Hence

$$B_2=\frac{1}{6} \qquad \ldots (80)$$

$$B_4=-\frac{1}{30} \qquad \ldots (81)$$

$$B_6=\frac{1}{42},\; B_8=-\frac{1}{30} \qquad \ldots (82$$

All these values agree with the results of Bernard & Child. Explicit formula for B_{2r+1} can be obtained by obtaining first a reoccurrence relation in B_{2r+1}, B_{2r-1} and then using matrices.

6. Relations between determinants of matrices $|A|$, $|D|$, $|E|$, $[\sigma][\sigma^1][N_r]$

6.a. The following relations can be obtained by comparing S_{2r} from (35) and (55)

$$\frac{|E_0{}^r|}{2r+1}\frac{\sigma^r\sigma^1}{2}+\frac{(-1)\,|E_1{}^r|\,\frac{\sigma^{r-1}\sigma^1}{2}}{(2r+1)\,(2r-1)}+\ldots=\frac{|D_0{}^{2r}|\,N_{2r}}{2r+1}-\frac{|D_1{}^{2r}|\,N_{2r-1}}{(2r+1)^{2r}}+\quad \ldots (83)$$

For $r=1$

we get

$$E_0^1\,(2n+1)=D_0^2\,(2n+4)-D_1^2 \qquad \dots \quad (84)$$

This is satisfied for values of E_0^1, D_0^2, D_1^2

6.b. In the same way the relation between A^1s & D^1s can be obtained by comparing S_{2r} from (14) and (55)

$$\frac{|A^r{}_0|}{r}\ \frac{\sigma^r}{2}+\frac{(-1)\,|A_1{}^r|}{r(r-1)}\ \frac{\sigma^{r-1}}{2}+\frac{(-1)^2\,|A^r{}_2|}{r(r-1)(r-2)}\ \frac{\sigma^{r-2}}{2}+\dots$$

$$=\frac{|D_0{}^{2r-1}|\,N_{2r-1}}{2r}-\frac{|D_1{}^{2r-1}|\,N_{2r-2}}{2r(2r-1)}+\dots \qquad (85)$$

$r=1$ gives

$$\frac{|A_0{}^1|\,\sigma}{2}=\frac{|D_0{}^1|\,N_1}{2} \qquad \dots \quad (86)$$

This is satisfied

$r=2$ gives

$$A^2{}_0\ \frac{\sigma^2}{4}-\frac{A_1{}^2\sigma}{2.2}=\frac{|D_1{}^3|\,N_3}{4}-\frac{|D_2{}^3|\,N_2}{6\cdot 3}+\frac{|D_3{}^3|\,N_1}{4\cdot 3\cdot 2} \qquad \dots \quad (87)$$

Which is satisfied to $A^2{}_0$, $A^2{}_1$, $D^3{}_1$, $D^3{}_2$.

7. Acknowledgements :

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VARIATION OF ANGLE OF CONTACT IN CAPILLARY TUBES OF LENGTH LESS THAN CAPILLARY RISE

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Introduction

When a capillary tube of height less than capillary rise is dipped in water the liquid fills the entire capillary tube leaving a small portion at the top. The liquid does not flow out.

If the capillary tube is sufficiently large the maximum rise will be obtained. The question naturally arises how the upward thrust is balanced in capillary tubes of less heights. It is experimentally observed that the angle of contact varies. The angle of contact in a tube of greater height maintaining capillary height is zero. As the height of the capillary tube is made less and less the angle of contact goes on increasing, it becomes 90° where there is zero height.

In this paper *Part A* consists of a relation between the length of tube (less than capillary height) and the *angle of contact* obtained mathematically, and *Part B* consists of experimental work carried out in support of mathematical results in *A*.

Part A

Let

h = capillary rise (Maximum) in a tube of radius r dipped vertically in water.

$x(<h)$ = height of water column when less height of tube is kept outside (measured from lowest point of meniscus).

We have the relation between surface tension (T) maximum capillary rise (h) angle of contact (λ) given by

$$T = \frac{r\left[h+\frac{r}{3}\right]\rho g}{2\cos\lambda} \quad .. (1)$$

Where ρ = density of liquid

g = Acceleration due to gravity.

When the tube of height ($x<h$) is dipped.

Let λ_x = Angle of contact.

The total upward thrust due to surface tension will be ($2\pi r\, T\cos\lambda_x$).

Force due to difference between the pressure and the weight of column of liquid $=\pi r^2(x+x')\rho g$ (where x' is due to liquid in meniscus).

Hence equilibrium will reduce to :

$$2\pi r\, T\cos\lambda_x = \pi r^2(x+x')\rho g$$

$$\cos\lambda_x = \frac{r(x+x')\rho g}{2T} \quad .. (2)$$

Substituting value of (1)

$$\cos\lambda_x = \frac{r(x+x')\rho g}{2\left[\dfrac{\left(r\left(h+\frac{r}{3}\right)\rho g\right)}{2}\right]}$$

$$\cos\lambda_x = \frac{x+x'}{h+\frac{r}{3}} \quad .. (3)$$

is calculated on assumption that the meniscus always remains spherical as the height of tube is reduced the centre of this sphere goes away from surface when

$$x \to 0$$
$$R_x \to \infty$$

Where R_x = Radius of sphere of which meniscus is the part.

Taking different values of x we will get a family of spheres which shall not be concentric.

The volume of the liquid above tangent plane to the meniscus is difference of volume of a cylinder height (h') and the volume inside a spherical cap of height h' whose base radius is r and the radius of sphere is R.

$$x' = \frac{h'}{2} - \frac{h'^3}{6r^2} \qquad \cdots (4)$$

(3) and (4) allow us to calculate λ_x for a given value of x.

For calculating x' from (4), we will require the value of h'. It can be experimentally obtained. The radius R_x of the sphere which contains the meniscus can be obtained by the formula.

$$R_x = \frac{r^2}{2h'} + \frac{h'}{2} \qquad \cdots (5)$$

We can also obtain the value of λ_x by the formula

$$\cos \lambda_x = \frac{r}{R_x} \qquad \cdots (6)$$

Thus (5) and (6) also allow us determine λ_x.

The value of λ_x, calculated by (3) and (4) or by (5) and (6) reduces to experimentally measuring h'.

Part 'B'

A capillary tube of radius 0.029 cm. was dipped vertically inside a vessel containing water. The maximum height of the capillary was found 4.706 cms. The use of travelling microscope was made.

The tube was then dipped further in the vessel so that the portions remaining above the water level in vessel was taken as 2.30 cms., 3.505 cms. and 3.732 cms. For all these values of $x's$, h' was measured with the help of travelling microscope. The results are tabulated as in the following table :

Sr.No.	x	h'	R_x	$\cos \lambda_x = \frac{x+x'}{h+\frac{r}{3}}$
				λ_x
1	2.30 cms	0.010 cms	0.047 cms	60° 54′
2	3.505 ,,	0.018 ,,	0.03236 ,,	40° 21′
3	3.932 ,,	0.024 ,,	0.02952 ,,	33° 18′

Conclusion

We could not take reading finer than those listed in the above table. However it is felt that R_x decreases as x increases R_x will tend to infinity as x tends to zero. We can also see that λ_x decreases as x increases. When $x \rightarrow 0$, $\lambda_x \rightarrow 90$ and when $x \rightarrow h \left[x' \rightarrow \frac{r}{3} \right]$ and $\lambda_x \rightarrow 0$.

The angle of contact for any height $x\,(<h)$ and radius of sphere R_x for $(x<h)$ can be obtained from the formulas in (3), (4), (5) and (6).

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FUNCTIONAL ANATOMY OF THE FEEDING APPARATUS OF THE WHITE-BACKED VULTURE GYPS BENGHALENSIS, GMELIN

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Introduction

The vultures are well known as Carrion–feeders and useful scavangers on the countryside and in the outskirts of town and villages. Once carcasses are detected, these birds drop one by one from seemingly empty sky. They demolish the carcasses with incredible speed and within short time a scattered collection of well stripped bones are left of carcasses. Due to such habits of vultures, they are of a great help where insanitory conditions exist. Such a specialization for feeding requires a great modification in the body form. This specialization in feeding ultimately reflects on the head architecture i.e. its skeleton and musculature. This paper deals with the adaptation of head structure for particular type of feeding of **Gyps benghalensis**, Gmelin. emphasizing on the structure of the bill, the tongue, the skull and the musculature.

Observations

The bill is very heavily built in this bird. It is compact and comparatively larger than normal flesh-eating birds. The upper beak is strong, well curved and pointed. The margins of both the beaks are sharp and blade like.

OSTEOLOGY

The skull of *Gyps* is schizognathous and holorhinal. It is of strong type with posterior oval cranium which is a little less than half the length of the skull. The foramen magnum faces backwards and downwards. The squamosal wing is very characteristic at the side and provides attachment surface for the jaw muscles. The exoccipitals along with basioccipital produce two blunt ventral processes. The zygomatic process is short and blunt. The tympanic cavity is large and is bordered by the squamosal wing. The frontals curve forward over the nasals laterally. The nasofrontal hinge is very well developed affording good degree of kinesis.

The orbit is large and rounded in shape. It is bounded posteriorly by postorbital process. It is arched by frontal margins and get additional protection by supraorbital process of prefrontal (lacrymal) dorsally. The anterior border is made of pars plana and the inferior and downward process of prefrontal. The antorbital process of the prefrontal and the orbital process of the quadrate form an incomplete floor. The interorbital septum is complete and is almost imperforate. The orbitosphenoid is completely ossified and is underlain by the basisphenoidal rostrum. The mesethmoid gives out lateral flat and triangular process, the pars plana which touches the inward pointed process of the inferior process of prefrontal.

The olfactory capsule is roofed by two fused nasals which are curved downwards laterally. The vomers are very small. The naris is in the form of an oblique, vertical oval aperture at the posterior end of the premaxilla. It is bounded posteriorly by nasal. The maxilla also contributes to form the ventral border of nares. The naris is holorhinal. The internasal septum is ossified and complete. Hence the nares are impervious. The ectethmoid touches the frontal and nasal dorsally. The antorbital vacuity lies between the naris and the orbit.

The bill is long, stout and heavy. The premaxilla curves very sharply downwards with a pointed tip at the anterior extremity. The upper jaw is made up of the usual bones and is typical of carnivorous birds. The jugal bar is strong and thick. The quadrate is well developed and movably articulated. The orbital process is flat and thin and is longer

than the otic process which articulates with the squamosal below the tympanic wing. The otic process is two headed and rests a cylindrical bearing articular surface of squamosal. This articulation permits a single plane rotation of the quadrate. All articulation of quadrate are dianthroses, The mandibular articulation with the foot of quadrate is a complex sliding rotation hinge (Bock, 64). The lateral condyle of the facet of quadrate is larger than the posterior one and is oval and rounded. The medial condyle is the largest and possesses an anterior lip, joining with corresponding lip of articular of lower jaw. The posterior condyle is small, curved and is continuous with the medial condyle. The pterygoid is short flat and twisted. It articulates with quadrate below the base of the orbital process and just above the lateral condyle. It approaches the palatines at an angle of 25°. The palatines occur as thin and broad horizontal plates which are parallel to each other. The outer edges and the posterior inner edges are curved ventralwards to surfaces for attachment of muscles. The choanae lies in between the palatines. The basipterygoid process is absent. The palate rests and slides along the basisphenoidal rostrum. The palatal processes of premaxillae fuse medially at the base of the beak. The maxillopalatine processes of maxillae approach each other towards the midventral line and they extend porteriorly above the palatines as thin flat processes. The palate is of the schizognathous type.

The lower jaw is comparatively broad and blade like and curved. It along with the upper beak constitutes a strong and powerful bill. The two rami of the mandible form a wide angle towards the symphysis which is long and quite distinct. Each ramus is of a single piece construction, being composed of five embryonic bones fused together indistinguishably (Yudin '61); (Lebdisnsky '18, '19, 20). The mandibular foramen is very minute. The angular is truncated. The surangular bears two foramina which are close by and it bears on the inner surface an elongated oval notch for the insertion of muscles. At the point of surangular foramen, the dorsal edge of mandible bends (slopes) downwards towards articular. The articular has a broad and wavy articulating surface. The internal process is long. The retroarticular process is well developed. The size and shape of this is correlated with depressor mandibulae muscle. The external process bears a tip which fits with the lip of median condyle of quadrate. Near the base of the internal

process is a small long elevation posteriorly which serves as a point of insertion of occipitomandibular ligament. On the medial side of the mandibular ramus is a small but distinct knob. This is the pseudotemporal process (Bock '64) *Hyoid apparatus :* This comprises a median series of skeltal elements and a pair of posterior horns or cornua. The median part consists of a pair of bones the paraglossa, a middle basihyal and a posterior urohyal. The paraglossa are curved upward laterally to give a deep spoon like shape to the tongue. They bear posteriorly cartilaginous flat extensions ceratohyals (anterior coruna). The paraglossa are wedged to the anterior triangular tip of the basihyal. The basihyal is stout, long and arrow head shaped. The urohyal is fused with the posterior edge of basihyal along the middle line. It also bears cartilaginous extensions. The posterior cornua are ankylosed with two dorsolateral facets at the posterior end of basihyal. Each cornua consists of four skeletal pieces (1) hypobranchial, (2) ceratobranchial, (3) epibranchial I and (4) epibranchial II. The median components form the main internal support of the tongue while the cornua support the ventrolateral parts of the floor of the mouth and also provide surfaces for the attachment of muscles of tongue and jaws.

The ligaments of the skull

The following ligaments have been found in the vultures:

1. Postorbital ligament: This extends from the postorbital process of the mandible just in front of the jaw articulation. It passes over the quadratojugal.
2. External jugomandibular ligament : This occurs as a short horizontally oblique band, extending from a notch of surangular posterolateral end of quadrate jugal opposite to jugal quadrate articulation. This lies over the ventral end of postorbital ligament.
3. Internal jugomaudibular ligament : Tnis extends from the jugal bar just beneath the postorbital ligament passes over the external process of articular, curves round the posterior end of quadrate and to the postero dorsal rim of articular.
4. Occipitomandibular ligament : This is a short and thick ligament extending between ventral tip of exoccipital portion of the typanic wing to the posterior edge of articular at the base of

the internal process of the mandible. This ligament also maintains the upward tension and keeps the quadrate articular articulation tight. (Davids '52; Goodman and Fisher '62.)

5. The lacrymojugal ligament : This occurs as a short strap extending between the ventral edge of the antorbital process of lacrymal and the dorsal rim of jugal bar. This only acts as a suspensory ligament of upperjaw.

MYOLOGY

The mandibular muscles

M. adductor mandibulae externus superficialis (a.m. ext. supf)

This is the most superficial muscle of all the adductors. It is a very heavily built muscle situated in the depression of the squamosal bone. The muscle covers the whole squamosal bone and a part of parietal. It has a fleshy origin but the fibres towards the origin have an aponeurotic outer surface. The muscle shows a pinnate arrangement. It runs anteriorly downwards towards the lower jaw.

The muscle fibres arise from the marginal ridge of the squamosal depression as well as from the lower marginal area of the squamosal bone. Though the muscle arises in a fleshy origin the uppermost layer of the muscle fibres near the origin show an aponeurotic nature. Most of the fibres converge in the middle. This tendon alongwith a few muscle fibres, runs downward. The slip, which arises in a fleshy origin beneath the postorbital process, becomes slightly aponeurotic after a small distance from its origin and joins with the tendon of the main mass.

The muscle runs downwards with a tendon in the middle and few fibres covering it. The muscle gets inserted on the dentary where, the tendinous slip inserts on the dentary whereas the fleshy muscle fibres get attached on the edge of the dentary.

M. adductor mandibulae externus medialis

This is also a well developed massive muscle assuming a triangular shape. The muscle is situated in-between the zygomatic process of the squamosal and the lower jaw. The anterior 2/3rd portion of the muscle is covered by the adductor mandibulae externus superficialis muscle.

The origin is in the form of a narrow tendinous ribbon from the zygomatic process of the squamosal. This tendinous ribbon becomes pinte type. The muscle becomes broader as it runs downwards.

The whole mass of the muscle becomes fleshy with muscle fibres. This broad mass of the muscle gets inserted on the outer surface of the dentary. The insertion extends more anteriorly and thus more than a half of the portion of lower jaw is covered by this muscle.

M. adductor mandibulae externus profundus

This is also well developed massive muscle assuming a triangular shape. The muscle is situated in-between the zygomatic, squamosal and the lower jaw.

This is the posterior most muscle of all the external adductors. The muscle is covered by M. adductor mandibulae externus medialis. The muscle has tendinous slips in the main mass and assumes a multipinnate structure. One of the tendons of this muscle arises very closely with the tendon of the adductor mandibulae externus medialis muscle. Due to these tendons the muscle is divided into an inner rostral slip and outer lateral slip. The rostral slip is ribbon like. Both the slips run downwards.

The muscle arises in a fleshy origin from the lower surface of the zygomatic process and the pro-otic bone. Fibres arising from its inner lateral side converge to a tendinous slip but the more internally situated fibres arising from the pro-otic, are attached to the tendon described above and assume a pinnate structure.

The muscle is inserted on the lateral side of the dentary just before the jaw-quadrate articulation.

M. adductor mandibulae medius

The main mass of the muscle is situated deeper than the external adductors. The muscle is well developed and massive. Muscle is situated as a thick strip of muscle mass in-between the sphenoidal bone and the lower jaw.

The margin of the muscle is slightly broad and fleshy with slightly aponeurotic upper surface. The tendon which is situated on the upper surface of the muscle runs downwards in the midst of the main mass

upto the insertion and due to this, outer surface of the muscle mass assumes a pinnate nature.

The muscle gets inserted fleshily on the inner lateral surface of the dentary slightly upper to the insertion of a.m. ext. superficialis and adjacent to the insertion of a.m. ext. profundus muscle.

M. adductor mandibulae internus

This muscle is very heavily built and further it consists of a dorsalis and a ventralis part. Both the parts are situated inbetween the palatine and the lower jaw.

M. adductor mandibulae internus dorsalis is the deepest of all the adductors and is massive. The muscle arises in a narrow fleshy origin from the dorsolateral surface of the palatine. It becomes broader as it runs downwards, backwards and inwards. The outer surface of the muscle runs downwards. This aponeurotic surface as well as the muscle becomes tendinous and narrow towards the insertion. The insertion is tendinous at the junction of angular and quadrato-articular joint. The a.m. intenus ventralis muscle arises from the anteroventral surface of the palatine. It runs downwards, backwards and comes out upto the outer surface of the lower jaw to get inserted. The origin is narrow and the insertion is broad and fleshy on outer surface of the dentary towards its hind end.

M. Pseudotemporalis

This is a massive, fan shaped muscle and runs from the quadrate to the inner surface of the hinder region of the lower jaw. This muscle consists of two strips.

The outer strip arises in partly aponeurotic and partly fleshy origin from the orbital process of the quadrate. The muscle runs downwards and becomes broad and gets twisted on the inner side. The inner slip arises from the main body of the quadrate and has a fleshy origin. The insertion is alongwith the earlier part.

M. sphenopterygoquadratus

This muscle is also situated very deeply. It has a palmate structure and runs from the orbital wall to the quadrate. The muscle arises in a broad fleshy origin from the sphenoidal bones just below the optic

foramen. The muscle becomes narrow as it runs downwards and inwards below the quadrate. The muscle gains an insertion on the inner surface of quadrate at its articulation with the lower jaw.

Discussion

The correlation of form and function is universal among animals. In highly specialized animals like birds, this aspect is very well studied by number of workers such as Burt (1930), Richardson (1942), Beecher (1951-a, 1951-b, 1953), Goodman and Fisher (1962), Zusi (1962) etc... have emphasized that a definite correlation exists between the morphology of the feeding apparatus and the feeding behaviour.

During my studies on the feeding apparatus of several birds (Dubale and Rawal, 1962, 1965, 1966, 1968-a, 1968-b and Rawal, 1966, 1968, 1969, 1970-a, 1970-b, 1970-c, 1971-a, 1971-b; 1971-c, 1972). I have observed that a definite muscle pattern and skeletal modifications are related to the diet of the birds. Though the pattern of the muscle remains almost same in all the birds, noteworthy differences are present as regards the nature of muscle its disposition and modifications of its skeletal elements which provide a seat for them.

The heavily built bill is a great weapon for the vultures for the food capture. These birds depend upon carrion food. To tear the flesh or for the removal of flesh from attachment with the bones, the pointed strong well curved bill is of great help to this bird. The margins of the bills are sharp and aid in cutting operation. The internal epidermal structures are well suited for engulping purpose.

During feeding the bird may come across with the bones along with flesh. At the time of parting the flesh from the bones these may strike on the roof of the cranium. The cranium is strong and hard to resist this strain. The ventral surface of the cranium is strengthened by heavy ossification of the respective bones. There is every chance of dis-articulation of the lower jaw due to heavy pressure of the upper jaw which is caused by strong adductor muscles. This is prevented by ligaments which are heavily tendinous. Even posterior slipover is also prevented by internal jugomandibular ligament during the process of tearing.

The muscles operating the bills are classified into :

1. The adductor group.

   This group includes the muscles responsible for raising the lower jaw :

   (*a*) adductor mandibulae externus muscles

   (*b*) adductor mandibulae medius muscle

   (*c*) dorsal division of the adductor mandibulae internus muscle.

2. The constrictor group
   Depressor mandibulae muscle

3. The protractor group
   Sphenopterygoquadratus muscle

4. The retractor group
   Ventral division of the adductor mandibulae internus muscle.

The bird requires though slow but tight grip over the flesh during tearing and cutting operation. The adductor muscles are modified for the purpose. The main muscle i.e. adductor mandibulae externus superficialis is of a partly parallel and partly pinnate type and is most massive with broad origin. Such a modification provides a slow and strong pull for raising the lower jaw. This is further enhanced by other muscles like m. adductor mandibulae externus medialis which is of a palmate type with narrow origin and broad insertion for pulling greater part of the lower jaw. The elevation of the hinder portion of the lower jaw is equally important, otherwise, there is every chance of disarticulation due to unequal pulling of the lower jaw. This is prevented by the two slips of adductor mandibulae externus profundus muscle. The adductor mandibulae internus helps in feeding operation by playing a dual role. This muscle acts as an adductor of the lower jaw and also as the retractor of the upper jaw. In this bird, the kinesis of the upper jaw is well marked and the function of the retraction has a significant role due to two parts of the internus muscle. The pseudotemporalis muscle also plays a dual role.

M. depressor mandibulae is very heavily built and shows a great degree of development. This feature assists the animal in widening the bill for the capture of large-sized flesh. When animal feeds on the large sized flesh, the beak is opened by the action of the depressor mandibulae

muscle upto certain extent. Further widening of the beak is caused by the elevation of the upper beak anterior to caniofacial hinge. This is done by the sphenopterygoquadratus muscle. This muscle is inserted at the junction of quadratojugal-articular joint. By the action of this muscle the quadrate is moved anteriorly at this pivot, this will force to the quadratojugal bar anteriorly and ultimately this bar which is joined anteriorly with the upper beak, will rock the beak at naso-frontal hinge and this will cause more elevation of the upper beak to facilitate the capture of large sized flesh.

Due to quick action of the adductor as well as abductor muscles, there is every chance of slip over of the mandibles causing disarticulation at quadrate joint. However, such a disarticulation is prevented by the tension caused by the external jugomandibular, ligament. The occipito mandibular ligament maintains an upward tension on the closed mandible and keeps the articulation tight.

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Explanation of Diagrams

White-backed Vultur—*Gyps benghalensis*, Gmelin

Fig. 1 : Lateral view of the skull.

Fig. 2 : Ventral view of the skull

Fig. 3 : Dorsal view of the skull

Fig. 4 : Ligaments of the skull

Fig. 5 : Lateral view of the superficial muscles of the jaws.

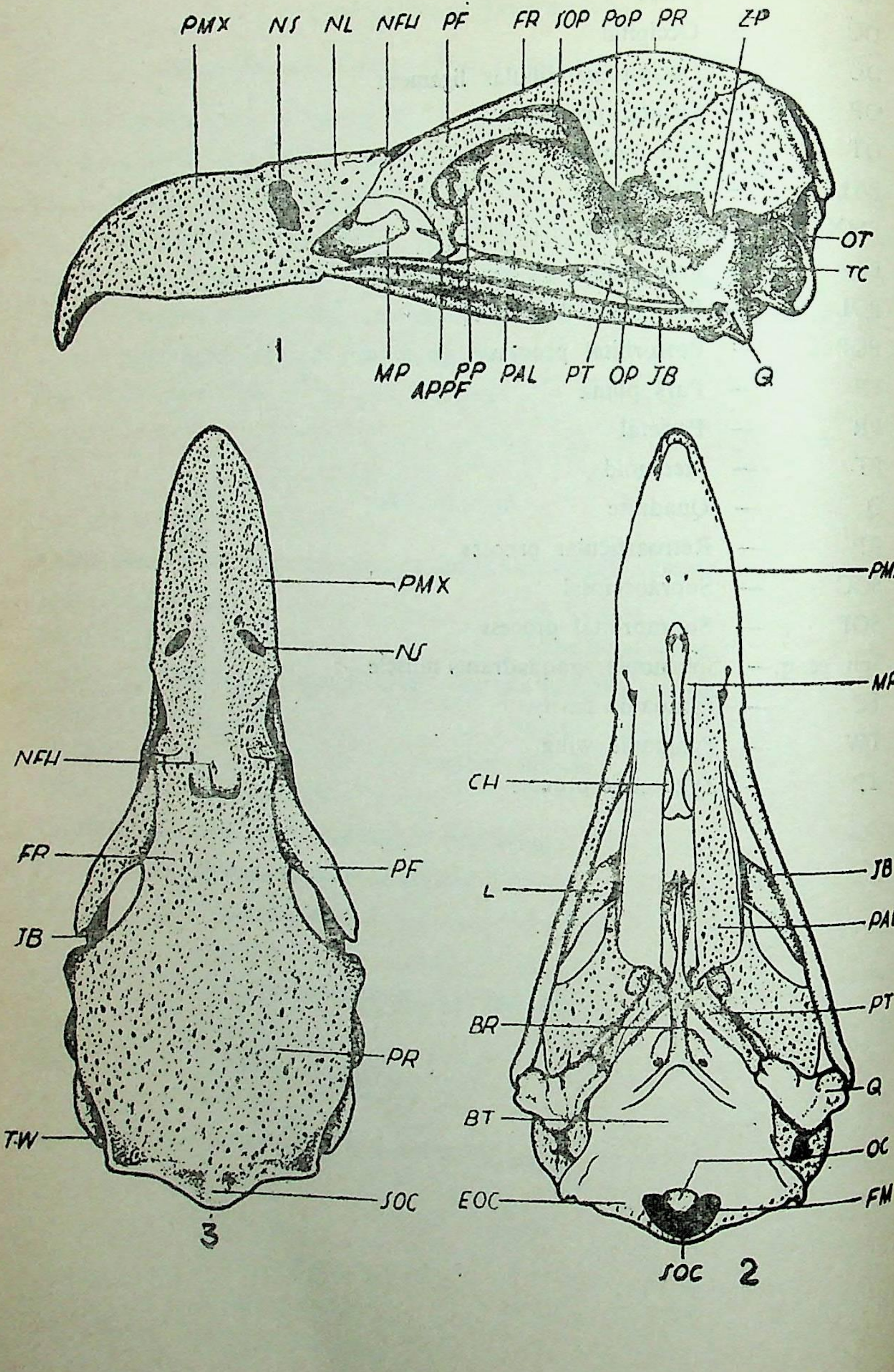
Fig. 6 : Deeper view of the muscles of the jaws after the removal of the superficial layer shown in figure 5.

Fig. 7 : Deepest view of the jaw muscles.

Abbreviations

AME. Med.—Adductor mandibulae externus medialis muscle
AME. Prof.— ,, ,, ,, profundus ,,
AME. Supf.— ,, ,, ,, Superficialis muscle
AMID —Adductor mandibulae internus dorsalis muscle
AMIV — ,, ,, ,, ventralis muscle
AMMed. — ,, ,, medius muscle
AP — Aponeurosis
AP PF — Antorbital process of prefrontal
BR — Basisphenoidal rostrum
BT — Basitemporal
CH — Choana
EJL — External jugomandibular ligament
EOC — Exoccipital
FM — Foramen magnum
FR — Frontal
IJL — Internal jugomandibular ligament
JB — Jugal bar
L — Lacrymal
LCJ — Lacrymojugal ligment
MP — Maxillopalatine
NFH — Nasofrontal hinge

NL — Nasal
NS — Nares
OC — Occipital
OL — Occipitomandibular ligament
OP — Orbital process
OT — Otic process
PAL — Palatine
PMX — Premaxilla
PF — Prefrontal
POL — Postorbital ligament
POP — Postorbital process
PP — Pars plana
PR — Parietal
PT — Pterygoid
Q — Quadrate
RP — Retroarticular process
SOC — Supraocciptal
SOP — Supraorbital process
Sph pt q.— Sphenopterygoquadratus muscle
TC — Tympanic cavity
TW — Tympanic wing
ZP — Zygomatic process.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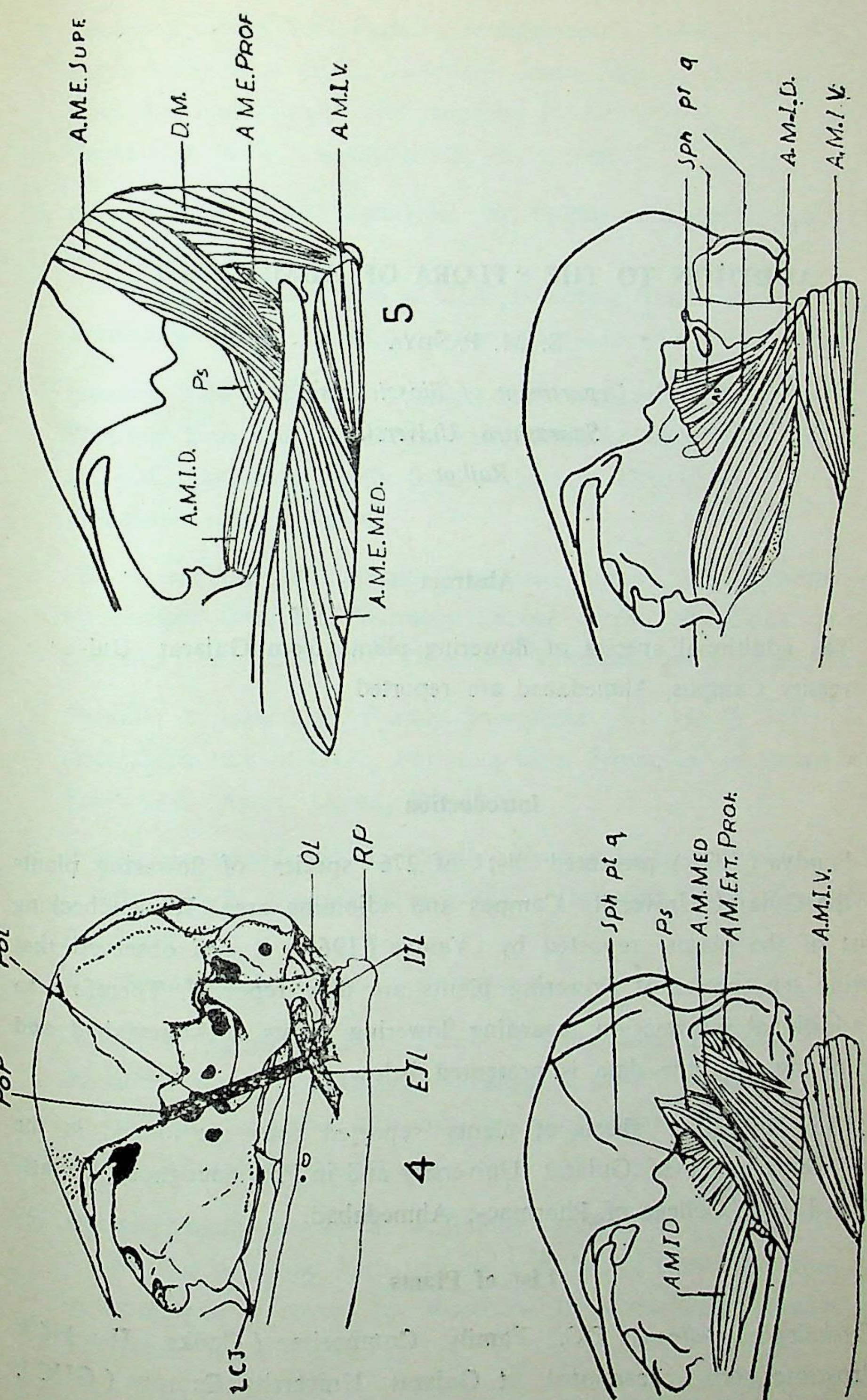
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ADDITION TO THE "FLORA OF AHMEDABAD"

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Abstract

Ten additional species of flowering plants from Gujarat University Campus, Ahmedabad are reported.

Introduction

Pandya (1972) presented list of 276 species of flowering plants from the Gujarat University Campus and adjoining area. While checking the list of the plants reported by Vaidya (1967) it was observed that following ten species of flowering plants are not reported. Therefore to give additional information regarding flowering plants of Ahmedabad and its adjoining area the data is presented below.

The herbarium sheets of plants reported here are lodged in the Botany Department of Gujarat University and in Pharmacognosy Department of L. M. College of Pharmacy, Ahmedabad.

List of Plants

1. *Tricholepis radicans* DC. Family Compositae (Cooke, II : 114). Prostrate herb, occassional at Gujarat University Campus (GUC), flowering from September to December.
   Vernacular name : Benthu-fusiarun.

2. *Lochnera pusilla* Sch. Family Apocynaceae (Cooke, II : 191). Erect herb, common at GUC, flowering from July to September; mostly dries out immediately after monsoon is over.
Vernacular name : Karapati-rai; Parvati-rai.

3. *Calotropis gigantea* (Linn.) R. Br. Family Asclepiadaceae (Cooke, II : 215).
A shrub, mostly rare at GUC, flowering from January to August.
Vernacular name : Rato-aankado; Moto-aankado.

4. *Ipomoea biloba* Forsk. Family Convolvulaceae (Cooke, II : 317). Prostrate herb with weak stem, rarely twining, leaves fleshy, occassional at GUC, flowering mostly from August to December.
Vernacular name : Aarvel.

5. *Datura innoxima* Mill. Family Solanaceae (Sutaria, 393). A shrub, probably escaped from the Pharmacy College garden, occassional at GUC, flowering from September to December. Vernacular name : Kala-dutara,

6. *Solanum Indicum* Linn. Family Solanaceae (Cooke, II, 336). Prickly undershrub rare at GUC, flowering from September to December.
Vernacular name : Dorali; Piludi.

7. *Boerhaavia repanda* Willd. Family Nyctaginaceae (Cooke, II, 564). Prostrate herb, occassional at GUC, flowering from September to December.
Vernacular name : Satodo; Punarnava.

8. *Euphorbia tirucalii* Linn. Family Euphorbiacea (Cooke, III : 66) Succulent shrub, occassional in hedges at GUC; probably introduced or cultivated and then escaped; flowering from August to October.
Vernacular name : Kharasani.

9. *Dactyloctenium sindicum* Boiss. Family Gramineae, (Cooke, III : 561). A prostrate perennial herb, common at GUC, flowering from August to December. Reported by Woodrow for Ahmedabad (Cooke, 1908).
Vernacular name : Chaman.

10. *Setaria rhachitricha* T. Cooke. Family Gramineae, (Cooke, III : 435). Erect herb, occassional at GUC, flowering in October to November.
Vernacular name : Kuṭra-ghas.

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AMINES AS CORROSION INHIBITORS FOR ALUMINIUM-57S IN HYDROCHLORIC ACID

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Abstract

O-anisidine, 2, 4, lutidine and hexamine are investigated as corrosion inhibitors for aluminium–57S in hydrochloric acid solutions. All the three substances are predominantly cathodic inhibitors and reduce the protective current The difference effect is negative in 2.0N HCl but becomes positive in the presence of inhibitors.

While a number of substances have been used as corrosion inhibitors for aluminium in hydrochloric acid, o-anisidine, 2, 4, lutidine and hexamine have not been used so far as inhibitors for the corrosion of aluminium and its alloys in hydrochloric acid solutions so far. It is well known that the change in the composition of the alloy may change the behaviour of the inhibitor. Many substances which are effective inhibitors for iron have been found to be ineffective for other metals. In the laboratory, aldehydes, ketones, amines and organic sulfur compounds are being investigated as corrosion inhibitors for different metals and alloys. This paper reports the performance of o-anisidine, 2,4 lutidine and hexamine as corrosion inhibitors for aluminium-57S in hydrochloric acid.

Aluminium alloy Indal–57 manufactured by M/s. Indian Aluminium Co., was selected for the study. It has the following composition :

Indal–57S halfhard; Cu traces, Si traces, Mg–2.0%, Mn 0.3%, Ti, traces remainder aluminium.

The preparation of specimens and corrosion studies were carried out as described in our previous publication.[1]

Observations :

The corrosion of aluminium–57S in hydrochloric acid increases with time as well as with acid concentration. The efficiency of inhibitors increases with an increase in inhibitor concentration and maximum protection is given at 43.5 ml./1 concentration of o–anisidine and 2,4 lutidine and 2.0% concentration of hexamine. The effect of time on inhibitor efficiency is given in Table 1.

TABLE 1

Effect of Time on Inhibitor Efficiency

Temperature : 35° ± 0.1°C

Inhibitor	*Inhibitor concen-tration in ml/1*	*Loss mg/dm²*	*% Efficie-ncy*	*Loss mg/dm²*	*% Effici-ency*	*Loss mg/dm²*	*% Effici-ency*	*Loss mg/dm²*	*% Effici-ency*	*Loss mg/dm²*	*% Effici-ency*
0.5N Hydrochloric acid		3 hours		6 hours		9 hours		24 hours		—	—
Nil		47.2	—	93.0	—	147.3	—	519.0	—	—	—
2, 4 pentanedione	17.4	15.2	67.8	26.0	72.0	35.5	75.9	91.1	82.5	—	—
2, 4 Lutidine	43.5	11.9	74.7	23.6	74.6	30.9	79.0	82.4	84.1	—	—
Hexamine	2.0%	11.7	75.3	18.2	80.5	28.2	80.9	78.1	84.9	—	—

1.0N Hydrochloric acid		10 minutes		30 minutes		60 minutes		120 minutes		180 minutes	
Nil		14.9	—	61.0	—	146.6	—	315.2	—	461.5	—
2, 4 Lutidine	43.5	7.3	47.3	19.2	64.4	44.2	69.9	81.3	74.2	93.5	79.7
o–anisidine	43.5	7.6	49.1	11.9	80.4	40.1	72.6	127.9	59.4	194.0	58.0
Hexamine	2.0%	3.0	80.0	8.7	85.8	17.6	88.0	77.2	75.5	185.1	59.9
2.0N Hydrochloric acid		5 minutes		10 minutes		15 minutes		30 minutes		60 minutes	
Nil		15.2	—	138.2	—	371.0	—	983.7	—	3139.0	—
2, 4 Lutidine	43.5	13.8	9.2	30.3	78.0	69.4	81.3	361.0	63.3	783.2	75.1
o–anisidine	43.5	6.8	55.4	14.6	89.4	40.4	89.1	297.3	69.8	481.0	84.7
Hexamine	2.0%	6.2	58.9	40.1	71.0	59.9	83.9	401.1	59.2	1018.0	67.6
3.0N Hydrochloric acid		5 minutes		10 minutes		15 minutes		30 minutes		—	—
Nil		459.9	—	2476.0	—	5226.0	—	—	—	—	—
2, 4 Lutidine	43.5	28.7	93.8	235.2	90.5	667.7	87.2	2054.0	—	—	—
o–anisidine	43.5	15.7	96.6	173.4	93.0	549.6	89.5	2075.0	—	—	—
Hexamine	2.0%	16.3	94.3	129.5	94.8	221.7	95.8	2089.0	—	—	—
4.0N Hydrochloric acid		1 minutes		2 minutes		5 minutes		10 minutes		—	—
Nil		29.0	—	306.2	—	5625.0	—	—	—	—	—
2, 4 Lutidine	43.5	4.6	84.1	23.8	92.2	270.2	93.4	1592.0	—	—	—
o–anisidine	43.5	3.3	88.8	25.8	91.6	240.1	95.7	2531.0	—	—	—
Hexamine	2.0%	4.1	86.0	23.9	92.2	153.7	97.2	3825.0	—	—	—

The influence of c.d. on the cathode and anode potentials of Al–57S in 1.0N hydrochloric acid and in the presence of o–anisidine, 2,4 lutidine and hexamine is shown in Figure 1.

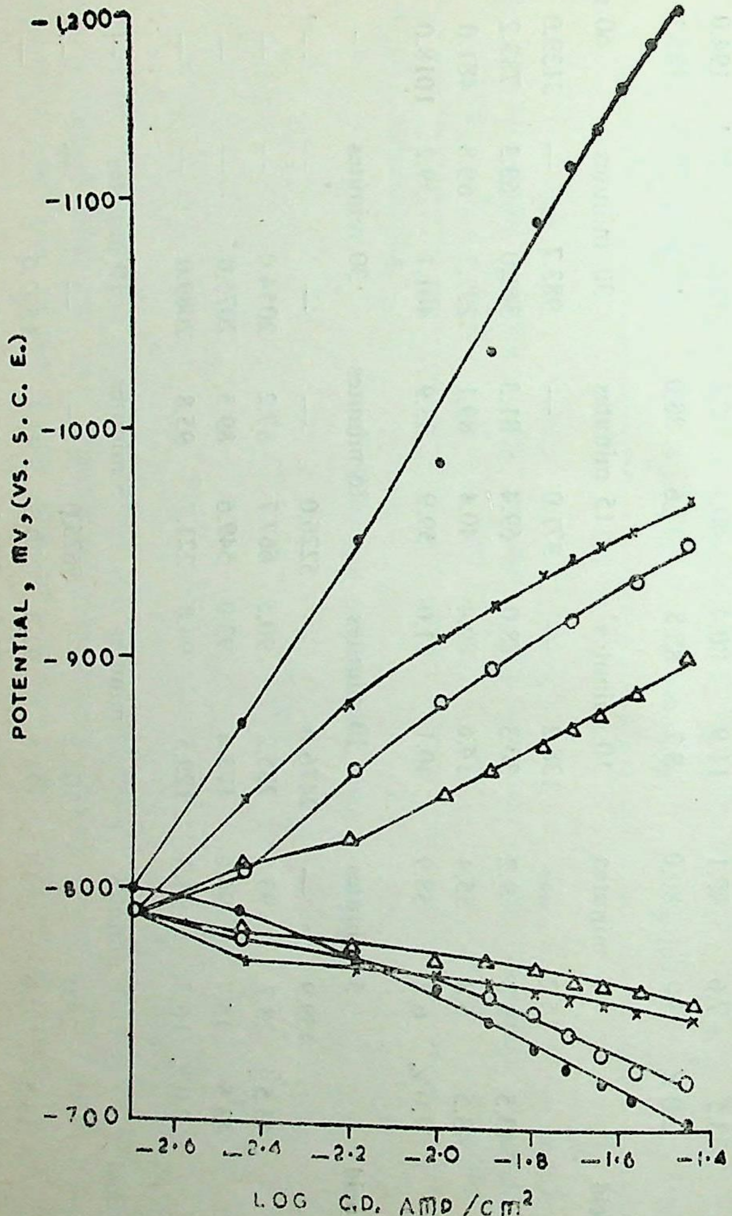

Fig. 1 : Influence of current density on the cathode and anode potentials of aluminium–57S in 1.0N hydrochloric acid in the presence and absence of inhibitors

●—● 2, 4 lutidine
×—× o–anisidine
△—△ hexamine
○—○ uninhibited 1.0N HCl

2,4 Lutidine :

2,4 lutidine is a good inhibitor, the efficiency ranging from 47–79, 8–81, 87–83 and 84–93% in 1.0, 2.0, 3.0 and 4.0N solutions of hydrochloric acid during the periods of study. The performance of 2, 4 lutidine improves with increase in acid concentration, both for five and ten minutes durations.

Addition of 2, 4 lutidine brings about a significant increase in cathode polarisation and the anode polarisation is also increased.

O--anisidine :

In 1.0 and 2.0N hydrochloric acid, there is no immediate effect of o-anisidine, but in 3.0N and 4.0N hydrochloric acid solutions the effect of inhibitor is felt immediately. For five minutes and ten minutes durations, the efficiency increases with increase in acid concentration.

O-anisidine increases the polarisation of cathode. Upto 1.948×10^{-2} amp./cm^2., there is a slight increase in anode polarisation subsequently, however, the shift in anode potential during anode polarisation is less than that in uninhibited 1.0N hydrochloric acid.

Hexamine :

In 1.0 and 2.0N solution of hydrochloric acid, the efficiency of hexamine ranges from 59.8% and 59.8% respectively. In 3.0N hydrochloric acid it is nearly constant at 95%. In 4.0N hydrochloric acid the efficiency improves with the passage of time (86.9%). For five minutes duration, the efficiency of hexamine improves with increase in acid concentration.

In the presence of hexamine the shift in cathode potential during polarisation, is less than that in uninhibited hydrochloric acid. The same is true for anode side also.

In the literature we have come across a reference[2] in which 3 amino pyridine at 10^{-2} M/liter concentration has no inhibitor effect although it does modify the cathode polarisation curve.

The value of Talel parameters, and the efficiencies of the inhibitor in 1.0N HCl evaluated from (1) extrapolation of cathodic Tafel line to the open circuit potential and (2) from the intersection of cathodic and anodic Tafel lines at the open circuit potential are shown in Table 2.

TABLE 2

Tafel Parameters and Efficiency of Inhibitors

Inhibitor and Inhibitor Concentration	*Tafel Slope b*		*Energy Transfer Coefficient*	*Corrosion current*				
	Anodic (Volts)	*Cathodic (Volts)*	*Cathodic*	*from Extrapolation of cathodic Tafel Line*	*from intersection of cathodic and anodic lines at open circuit potential*	*Inhibitor Efficiency from (6)*	*Inhibitor Efficiency from (7)*	*Inhibitor Efficiency from loss in weight method*
Nil	0.12	0.15	0.41	3.57×10^{-3}	5.32×10^{-3}			
2, 4 Lutidine (43.5 ml/1)	0.11	0.22	0.28	1.14×10^{-3}	1.62×10^{-3}	69.0	69.5	47–74
o–anisidine (43.5 ml/1)	0.07	0.20	0.30	7.31×10^{-4}	1.62×10^{-3}	79.5	69.5	49–80
Hexamine (2.0%)	0.05	0.12	0.51	5.68×10^{-4}	1.62×10^{-3}	84.0	69.5	75–88

Plots of log aluminium surface coverage against log inhibitor concentration show that Freundlich adsorption low is obeyed by the inhibitors.

The activation energies of the inhibitors were evaluated from plots of 1/T against log corrosion rates according to the Arrhenius equation. Results are given in Table 3.

TABLE 3

Activation energies in the presence and absence of inhibitors

(In K-Cal./mole)

Inhibitory	30 *minutes*	60 *minutes*	120 *minutes*	180 *minutes*
Nil	13.8	12.0	11.96	11.96
2, 4 lutidine	11.34	9.21	8.75	10.59
0-anisidine	13.74	7.37	7.37	6.44
Hexamine	18.42	25.8	33.2	20.04

The activation energies of inhibited reaction at high coverages can be either larger or smaller than the uninhibited reaction. Machu[3] had reported that for powerful inhibitors, the activation energy is lower for inhibited than for uninhibited reaction. This type of behaviour has been explained by Putilova[4] as due to an increase in surface area of metal covered by inhibitor molecules as the temperature rises. However Riggs[5] suggested that at high coverages the extent of adsorption is no longer rate determining.

Studies of cathodic protection to aluminium-57S in 2.0N hydrochloric acid indicate that the addition of inhibitors considerably lowers the protective current (Table 4).

TABLE 4

Effect of current density on cathode weight loss (cathodic protection)

Aluminium-57S	*Current density amp./dm²*	*weight loss mg./dm²*	*Protection % current*	*due to current⁺ Inhibitor*
Nil	0.0	1071.0	—	—
	0.081	984.0	8.0	—
	0.162	682.0	36.2	—
	0.325	552.6	48.4	—
	0.487	360.2	66.4	—
	0.650	180.9	83.1	—
	0.812	0.0	100.0	—
2, 4 lutidine 43.5 ml/l	0.0	381.5	—	64.4
	0.325	141.8	62.8	86.8
	0.487	57.1	85.0	894.7
	0.520	0.0	100.0	100.0
0—anisidine 43.5 ml/l.	0.0	304.0	—	71.6
	0.325	177.6	41.6	83.4
	0.406	96.2	68.4	91.0
	0.487	0.0	100.0	100.0
Hexamine 2.0%	0.0	422.2	—	60.6
	0.487	149.9	64.4	86.0
	0.568	57.1	86.5	94.8
	0.650	0.0	100.0	100.0

Results obtained under external anodic current show that the difference effect is negative for aluminium-57S in 2.0N hydrochloric acid, whereas in the presence of inhibitors, the difference effect becomes positive. The values of difference effect coefficient were evaluated according to the equation :

$$\text{KDE} = \frac{\triangle \text{ i Corr}}{\triangle \text{ i Pol}}.$$

The values of KDE in uninhibited 2.0N hydrochloric acid in the presence of 43.5 ml./l. 2,4 lutidine, 43.5 ml./l. o-anisidine 2.0% hexamine are-10.3, +0.71, +0.70 and +0.80 respectively.

Difference effect being positive in the presence of inhibitors may be associated with the hindered adsorption of chloride ions. It is known that the adsorption of halogen ions aids anodic dissolution of metal. Thus in the presence of the inhibitors, the dissolution of the oxide layer is delayed.

Acknowledgement

We thank the authorities of Gujarat University for research facilities.

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THE FLORA OF GUJARAT STATE

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Ahmedabad

Introduction

The present Gujarat State consists of three regions—Gujarat, Kutch and Saurashtra. Here and there scattered information about the plants growing in our area have been recorded as the labour of love by various persons engaged in various branches of the public services. The necessity for local or regional floras to supplement Cooke's (1903–1908) work was recognised to prepare such floras. In this connection Saxton and Sedgwick (1918), Blatter (1908 & 1909), and Thakar (1910) took the lead for Gujarat, Kutch and Saurashtra respectively. In the year 1926 Thakar published in Gujarati an elaborate treatise on the plants of Kutch and their utility. To this further additions are made by Puri et al (1960). Under the patronage of the Saurastra Research Society, Santapau (1962) has published the Flora of Saurashtra, Part I, and the manuscript of the remaining part is handed over to the University of Saurashtra for publication which is anxiously awaited for. The Flora of Saurastra–a check-list is published by Santapau and Janardhanan (1966). Further impetus to enhence this work in Gujarat is given by Gujarat Research Society and also by the Staff of the Botany Departments of various Universities and Colleges in Gujarat State.

The present paper is based on the data obtained by analysing the various available publications up to the year 1970.

Statistical Synopsis

The flora comprises of 156 families, 758 genera and 1716 species. Table I gives the number and percentage of families, genera and species in each class.

TABLE 1

	Dicotyledons		Monocotyledons		Total
	No.	%	No.	%	
Family	125	80.128	31	19.872	156
Genera	581	76.65	177	23.35	758
Species	1284	74.826	432	25.174	1716

The ratio of Monocotyledons to Dicotyledons is 1:2.972 of species, 1:3.282 of genera and 1:4.032 of families. The ratio of the genera to species is 1:2.44. The ratio of the family to genera is 1:4.86 and that of the family to species is 1:11.00. The ratio of the family to genera of dicotyledons is 1:4.65. while that of the species is 1:10.27. The ratio of the family to genera of Monocotyledon is 1:5.70 while that of the species is 1:13.93. The ratio of the genera to species of Dicotyledon and Monocotyledon are 1:2.21 and 1:2.44 respectively. This shows the small proportion of species to the number of genera and families.

Except for the families Gramineae Juss., Cyperaceae Juss., and Orchi daceae Juss., the Monocotyledons are very poorly represented. Of the 432 species of Monocotyledons 340 belong to the above three families, while the remaining 92 species belong to 28 different families.

Of the 1284 species of Dicotyledons 750 belong to 12 families. They are Papilionaceae Giseke., Compositae Geiscke., Malvaceae Juss., Convolvulaceae Juss., Euphorbiaceae Juss., Acanthaceae Juss., Caesalpinaceae R.Br., Mimosaceae R.Br., Cucurbitaceae Juss., Labiatae Juss., Rubiaceae Juss., and Scrophulariaceae Juss. The remaining 534 species belong to 113 different families.

Of the 156 families 73 have one genus, 22 have two genera, 12 have three genera, 12 have four genera, 4 have five genera, 3 have six genera, 3 have seven genera, 2 have eight genera, 4 have nine genera and 5 have ten genera. The remaining 16 families have genera more than 10 varying from eleven to ninty-five genera.

Of the 73 families 47 have one genus and one species i.e. monotypic, 14 have one genus and two species i.e. ditypic. The remaining 12 families have genera varying from 3 to 9 species. Hence there are more number of monotypic and ditypic families.

Of the 758 genera 481 have one species, 122 have two species and the remaining 155 genera have species varying from **3 to 41.** Hence there are more number of monotypic and ditypic genera.

The genera having more than ten species are Cyperus Linn., Ipomea Linn., Cassia Linn., Crotalaria Linn., Indigofera Linn., Hibiscus Linn., Fimbristylis Vahl., Eragrostis Beauv., Euphorbia Linn., Acacia Mill., Tephrosea Pers., Alysicarpus Neck. Scirpus Linn., and Ficus Linn., with 41, 24, 21, 20, 20, 17, 17, 17, 16, 15, 13, 12, 12 and 11 species respectively. With the exception of Ficus Linn., remaining 13 genera belong to one or the other of the 21 largest families. Of the above 13 genera 4 belong to the family Papilionaceae Giseke., and 3 to Cyperaceae Juss. The remaining 6 genera belong to 6 families e.g. Convolvulaceae Juss., Caesalpiniaceae R.Br., Mimosaceae R.Br., Euphorbiaceae Juss., Malvaceae Juss., and Gramineae Juss., The family Moraceae Link is only family to which genus Ficus Linn., belongs is not included in the 21 largest families.

The largest families in genera and species along with the number of genera and species and their places are given in table II

TABLE II

Genera 1	*Place* 2	*Families* 3	*Families* 4	*Place* 5	*species* 6
95	1	Poaceae Gramineae	Poaceae Gramineae	1	234
52	2	Fabaceae Papilionaceae	Fabaceae Papilionaceae	2	175
50	3	Asteraceae Compositae	Asteraceae Compositae	2	175
26	4	Acanthaceae	Cyperaceae	3	84
20	5	Scrophulariaceae	Malvaceae	4	61
20	5	Euphorbiaceae	Convolvulaceae	5	50
18	6	Rubiaceae	Euphorbiaceae	6	47
15	7	Malvaceae	Acanthaceae	7	44
15	7	Cucurbitaceae	× Caesalpiniaceae	8	40
14	8	Asclepiadaceae	Mimosaceae	9	34
14	8	Labiatae	Cucurbitaceae	10	33

1	2	3	4	5	6
13	9	Sterculiaceae ×	Labiatae	11	31
13	9	Mimosaceae	Rubiaceae	12	30
11	10	Brassicaceae Cruciferae	Scrophulariaceae	12	30
11	10	Convolvulaceae	Brassicaceae Cruciferae	13	50
11	10	Orchidaceae	Amaranthaceae	13	25
10	11	Apiaceae Umbelliferae ×	× Boraginaceae	14	22
10	11	Bignoniaceae ×	Orchidaceae	14	22
10	11	Verbenaceae ×	× Tiliaceae	15	21
10	11	Amaranthaceae	Asclepiadaceae	15	21
10	11	Cyperaceae	× Solanaceae	16	20
448					1224

From the above table it is seen that there are 21 families with genera varying from 10 to 95 and species varying from 20 to 234. There are certain families which do not fit in the genera and the species columns. There are Sterculiaceae Vent., Umbelliferae Juss., Bignoniaceae C. A. Agardh and Verbenaceae Jaume St. Hill with 16, 12, 10 and 14 species respectively i.e. they have less than 20 species; while Caesalpiniaceae R. Br., Boraginaceae Juss., Tiliaceae Juss., and Solanaceae Juss., with 9, 8, 4 and 9 genera respectively i.e. they have less than 10 genera. Some of these families have retained their rank while others have higher or lower rank and this can be seen from their place number.

Of the 21 largest species families the first three families make up one-third, the first-eight one-half and the first twenty-one three-fourth of the total flora; where as the remaining one-fourth is comprised in 135 families. Of the largest genera families make up nearly 60% of the total genera while the remaining 40% is comprised in 135 families.

Comparisons

Various authors have assigned various terms for the phytogeographical divisions and vegetation of our area. Most of them are briefly described by the author (1950); but few more are given here.

Chatterjee (1962) has revised phytogeographical regions of Hooker (1904) and it is interesting to note that the present Gujarat State comes under Indus Plain and Malabar regions as previously recorded by Hooker. Further this knotty problem of vegetation is elucidated by the members of Institute Francais of Pondichiry in terms of "bioclimates". Good deal of information can be obtained about Gujarat State with reference to Legris and Viart (1959). Bagnouls and Meher-Homji (1959) and Meher-Homji (1963). Good (1965) plate 4 of the floristic regions of the World shows Kutch as African-Indian desert and the rest as Indian; In Good (1965) plate 2 of the vegetation map of the World by Rübel Kutch is shown as desert and semi-desert, grassland in Saurashtra and Northern Gujarat while forest and woodland in Southern Gujarat.

In table III comparison is made of 21 largest families of Gujarat State with 10 largest families of British India and 24 largest families of the World as cited by Hooker (1904) and Good (1965) respectively.

TABLE III

Families

Place 1	*Br India* 2	*Gujarat State* 3	*World* 4
1	Orchidaceae	Poaceae Gramineae	Compositae
2	Leguminosae	Fabaceae Papilionaceae	Orchidaceae
		Asteraceae Compositae	
3	Gramineae	Cyperaceae	Papilionaceae
4	Rubiaceae	Malvaceae ×	Rubiaceae
5	Euphorbiaceae	Convolvulaceae ××	Gramineae
6	Acanthaceae	Euphorbiaceae	Euphorbiaceae
7	Compositae	Acanthaceae	Labiatae
8	Cyperaceae	Caesalpiniaceae	Scrophulariaceae
9	Labiatae	Mimosaceae	Cyperaceae
10	Urtecaceae ×	Cucurbitaceae ×	× Melastomataceae
11		Labiatae	× Myrtaceae

1	2	3	4
12		Rubiaceae Scrophulariaceae	Ascl. , iadaceae
13		Brassicaceae Cruciferae	Acanlhaceae
14		Amaranthaceae × Boraginaceae × Orchidaceae	× Umbelliferae
15		Tiliaceae × Asclepiadaceae	× Liliaceae
16		Solanaceae	Cruciferae
17			Solanaceae
18			× Ericaceae
19			× Piperaceae
20			× Apocynaceae
21			× Rosaceae
22			Mimosaceae
23			× Palmae
24			× Araceae

From the above table it is seen that there are some families which do not fit in these columns. They are Urticaceae Juss (10, 25), Malvaceae Juss. (18, 64), Convolvulaceae Juss. (12, 53), Caesalpiniaceae R. Br. (9, 40), Cucurbitaceae Juss. (15, 33), Amaranthaceae Juss. (10, 25), Boraginaceae Juss. (8, 23), Tiliaceae Juss. (4, 21), Melastometaceae Juss. Myrtaceae Juss. (4, 6), Umbelliferae Juss. (10, 12), Liliaceae Juss. (8, 11), Ericaceae Juss., Piperaceae C. A. Agardh, Apocynaceae Juss. (9, 12), Rosaceae Juss. (1, 1), Palmaceae Juss. (7. 7) and Araceae Juss. (8, 9). Families which are represented in the flora of Gujarat State are shown here with the number of genera and species in brackets. Families having higher or lower rank can be seen from their place number. Chorwad is famous for its betel leaf, yet it is not recorded by Santapau and Janardhanan (1966).

Chatterjee (1939) differing from Hooker (1904) has given 15 largest families of dicotyledons only. In the table IV comparison is made of

these largest dicotyledonous families of the state with that of India and the World.

TABLE IV

Dicotyledonous Families

Place	*Br. India*	*Gujarat State*	*World*
		Fabaceae	
1	Papilionaceae	Papilionaceae	Compositae
		Asteraceae	
		compositae	
2	Compositae	Malvaceae ×	Papilionaceae
3	Rubiaceae	Convolvulaceae	Rubiaceae
4	Acanthaceae	Euphorbiaceae	Euphorbiaceae
5	Euphorbiaceae	Acanthaceae	Labiatae
6	Labiatae	Caesalpiniaceae ×	Scrophulariaceae
7	Scrophulariaceae	Mimosaceae	× Melastomataceae
8	Rosaceae ×	Cucurbitaceae ×	× Myrtaceae
9	Balsamindceae ×	Labiatae	Asclepiadaceae
10	Asclepiadaceae	Rubiaceae	Acanthaceae
		Scorphulariaceae	
		Brassicaceae	
11	Primulaceae ×	Cruciferae	× Umbelliferae
		Amaranthaceae ×	
12	Gentianaceae ×	Boraginaceae ×	Cruciferae
13	Umbelliferae ×	Tiliaceae ×	Solanaceae
		Asclepiadaceae	
14	Cruciferae	Solanaceae	× Ericaceae
15	Convolvulacae	Lythraceae ×	× Piperaceae
16			× Apocynaceae
17			× Rosaceae
18			Mimosaceae.

In the above table families which do not fit in these columns are Rosaceae Juss. (1, 1), Balsaminaceae DC. (1, 4). Primulaceae Vent., (1, 3), Gentianaceae Juss. (7, 18), Umbelliferae Juss, (10, 12). The family Lythraceae Jaume St Hill, (6, 19) is in addition to already stated families in table III. Families having higher or lower ranks can be seen from their place number.

Of the 24 World largest families 18 belong to Dicotyledonous and 6 to Monocotyledonous families. The comparison of 8 largest Monocotyledonous families is given in table V. Families representing India are from Maheshwari et al (1965).

TABLE V

Monocotyledonous Families

Place	*Br. India*	*Gujarat State*	*World*
1	Orchidaceae	Poaceae Gramineae	Orchidaceae
2	Gramineae	Cyperaceae	Gramineae
3	Cyperaceae	Orchidaceae	Cyperaceae
4	Liliaceae	Liliaceae	Liliaceae
5	Araceae	Commelinaceae	Palmaceae
6	Palmaceae	Araceae	Araceae
7	Commelinaceae	× Zingiberaceae	
8	Juncaceae ×	Palmaceae	

The only family Liliaceae Juss., has maintained remarkably its rank in all the three. The others have higher or lower rank. The families Juncaceae Juss (1, 1) and *Zingiberaceae* Lindle. (4, 8) do not fit in are given with genera and species numbers in brackets.

Table VI gives the percentages of families, genera and species of Dicotyledons and Monocotyledons of Gujarat State and its two regions Kutch and Saurashtra.

TABLE VI

	Dicotyledons			*Monocotyledons*		
	Families	*Genera*	*Species*	*Families*	*Genera*	*Species*
Gujarat State	80.128	76.650	74.826	**19.872**	**23.350**	**25.174**
Kutch 1926	86.666	80.064	81.978	13.333	19.935	18.020
Kutch 1960	**83.69**	**80.38**	**81.30**	16.31	19.62	18.70
Saurashtra 1910	82.76	84.91	85.55	17.24	15.09	14.45
,, 1966	81.39	78.85	77.80	18.61	21.15	22.20
North Gujarat	84.61	81.08	73.74	15.39	18.92	26.26

From the above table it is seen that there is gradual increase in the percentage of families, genera and species of Dicotyledons from Gujarat State to Saurashtra and then to Kutch. The percentage of families, genera and species of Monocotyledons there is gradual increase from Kutch, Saurashtra and Gujarat State. The highest percentage is shown in bold types. Further it is seen that in case of Kutch and Saurashtra of 1960 and 1966 respectively there is decrease in the percentages of Dicotyledons while there is increase in the percentages of Monocotyledons.

Table VII gives various ratios.

TABLE VII

1	*Gujarat State* 2	*Kutch* 1926 3	*Kutch* 1960 4	*Saurashtra* 1910 5	*Saurashtra* 1966 6	*North Gujarat* 7
Ratio of Monocotyledon to Dicotyledon of Species	1:2.972	1:4.549	**1:4.353**	1:5.92	1:3.50	1:2.81

1	2	3	4	5	6	7
Ratio of Monocotyledon to Dicotyledon of Genera	1:3.282	1:4.016	**1:4.097**	1:5.63	1:3.73	1:4.28
Ratio of Monocotyledon to Dicotyledon of Families	1:4.032	1:6.5	**1:5.57**	1:4.8	1:4.37	1:5.5
Ratio of Genera to Species	**1:2.44**	1:1.82	1:1.73	1:1.76	1:1.97	1:1.83
Ratio of Family to Genera	**1:4.86**	1:4.16	1:3.99	1:3.88	1:4.66	1:4.06
Ratio of Family to Species	**1:11.00**	1:7.54	1:6.92	1:6.88	1:9.02	1:7.45

It is seen that the Gujarat State has highest ratio of genera to species, family to genera and family to species. Kutch has the highest ratio of Monocotyledon to Dicotyledon of species, genera and families. These are also shown in bold types. For the sake of comparison previous years figures are also given for Kutch and Saurashtra.

In Table VIII—A and B the largest families with place and percentage of total for Gujarat State, Kutch and Saurashtra, are given.

TABLE VIII—A

Families	*Place* Gujarat State	Kutch 1926	Kutch 1960	Saurashtra 1910	Saurashtra 1966	North Gujarat
Acanthaceae	8	7	7	6	**5**	6
Amaranthaceae	12	9	**8**	10	13	10
Asclepiadaceae	14	11	14	8	**12**	12
Boraginaceae	13	9	**10**	9	11	10
Capparaceae	—	8	**12**	11	15	13
Chenopodiaceae	—	14	—	13	16	—
Compositae	**3**	3	**3**	3	**3**	4
Convolvulaceae	6	5	**5**	5	**5**	5
Cruciferae	12	—	—	—	—	—
Cucurbitaceae	**9**	8	**9**	7	**9**	8
Cyperaceae	**4**	6	6	13	7	3
Euphorbiaceae	7	8	**6**	5	**6**	5
Ficoideae	—	14	—	15	17	15
Gramineae	**2**	2	**2**	2	**2**	1
Labiatae	**10**	12	15	8	**10**	11
Leguminosae	**1**	1	**1**	1	**1**	2
Liliaceae	—	—	—	13	16	—
Malvaceae	5	4	**4**	4	**4**	7
Orchidaceae	13	—	—	—	—	—
Rubiaceae	11	—	—	9	**8**	14
Scrophulariaceae	11	15	—	14	**10**	8
Solanaceae	15	13	13	12	**8**	13
Tiliaceae	14	10	14	8	**13**	9
Verbenaceae	—	15	**11**	14	13	—
Urticaceae	—	—	—	14	14	—
Palmaceae	—	—	—	14	17	—
Apocynaceae	—	—	—	15	16	—
Total..	19	20	17	25	25	19
Families	156	75	92	87	129	91
Genera	758	311	367	338	602	370
Species	1716	566	637	595	1185	678

TABLE VIII–B

Percentages

Families	*Gujarat State*	*Kutch 1926*	*Kutch 1960*	*Saurashtra 1910*	*Saurashtra 1966*	*North Gujarat*
Acanthaceae	2.56	3.53	3.30	3.02	**3.79**	3.24
Amaranthaceae	1.46	2.82	**2.98**	2.01	1.51	1.91
Asclnpiadaceae	1.22	2.12	**2.04**	2.35	1.68	1.62
Boraginaceae	1.28	2.82	**2.67**	2.18	1.77	1.91
Capparaceae	—	3.00	**2.35**	1.68	1.09	1.47
Chenopodiaceae	—	1.41	—	1.15	1.01	—
Compositae	**10.19**	6.53	8.64	6.22	5.23	4.27
Convolvulaceae	3.09	4.41	**3.92**	4.03	3.79	3.83
Cruciferae	1.46	—	—	—	—	—
Cucurbitaceae	1.92	3.00	**2.83**	2.85	1.94	2.65
Cyperaceae	**4.89**	4.06	3.45	1.15	2.87	6.63
Euphorbiaceae	2.74	3.00	3.45	4.03	**3.62**	3.83
Ficcideae	—	1.41	—	0.84	0.84	1.18
Gramineae	**13.64**	11.13	11.30	8.74	12.65	15.33
Labiatae	1.81	1.94	**1.88**	2.35	1.86	1.77
Leguminosae	**14.51**	15.54	12.21	20.67	14.17	13.56
Liliaceae	—	—	—	1.15	1.01	—
Malvaceae	3.73	5.30	**5.02**	5.21	4.72	3.09
Orchidaceae	1.28	—	—	—	—	—
Rubiaceae	1.75	—	—	2.18	**2.02**	1.30
Scrophulariaceae	1.75	1.23	—	0.98	**1.86**	2.65
Solanaceae	1.16	1.77	**2.20**	1.32	2.02	1.47
Tiliaceae	1.22	2.63	**2.04**	2.35	1.51	2.06
Verbenaceae	—	1.23	**2.51**	0.98	1.51	—
Urticaceae	—	—	—	0.98	1.35	—
Palmaceae	—	—	—	0.98	0.84	—
Apocynaceae	—	—	—	0.84	1.01	—
Total..	71.66	78.88	72.79	80.24	75.67	73.77

It is seen that there are families which do not fit in first fifteen place, some have kept their ranks, while others have high or low ranks. As regards percentages there is good deal of variation. The highest percentages of families are shown in bold types. It is observed that in case of some

families having high ranks have high percentage in the same region, e.g. Acanthaceae etc. In others it is not so, e g. Asclepiadaceae has high place in Saurashtra while high percentage in Kutch. In some families ranks are kept but not the percentages e.g. Compositae etc. These largest families vary from 17 of Kutch to 25 of Saurashtra. While their percentages vary from 71.66 of Gujarat State to 75·67 of Saurgshtra. In Kutch number of families decrease from 20 to 17 and the percentage is decreased from 78.88 to 72.79. In Saurashtra number of families remain the same i.e. 25 but the percentage is decreased from 80·24 to 75.67.

Although good deal of information about the flora of Gujarat region is available its comparison is postponed for the present as the work is still in progress at different places in Gujarat. At the same time as stated previously North Gujarat is included in tables VI, VII, VIII, but not compared.

Summary

Data for the proposed Flora of the Gujarat State are collected from the various available publications up to the year 1970. On this an account of the systematic statistical synopsis is given here and the comparisons are also made of its largest families with that of India and the World; of its Dicotyledonous and Monocotyledonous families with that of India and the World and finally with two of its three regions—Kutch and Saurashtra.

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NOTES ON THE FLORA OF SAURASHTRA

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Introduction

Not more than hundred species are recorded from different localities in Saurashtra in the Flora of the Presidency of Bombay by Cooke (1901-1908). But a complete and comprehensive account of the Flora of Barda mountain was published in Gujarati two years later by Indraji (1910). In order to bring this master piece in light the author published a brief account in the form of statistical synopsis in the year 1949. Recently in the year 1966 Santapau and Janardhanan has published the check list of the flora of Saurashtra. The arrangement and nomenclature adapted by Indraji is of Hooker (1875–97) while that of Cooke (1901–1908) by the author (1949). The cultivated plants are excluded from the then Flora while these are included in the recent one (1966).

The present note is based on the recent check list.

Statistical Synopsis

The flora comprises of 129 families, 602 genera and 1185 species of flowering plants, excluding Gymnosperms.

Of the 129 families 105 belong to Dicotyledons and the remaining 24 belong to Monocotyledons. Of the 602 genera 475 belong to Dicotyledons and the remaining 127 to Monocotyledons. Of the 1185 species 922 belong to Dicotyledons and the remaining 263 belong to Monocotyledons. The ratio of Monocotyledons to Dicotyledons is 1 : 3.50 of species, 1 : 3.73 of genera and 1 : 4.37 of families. The ratio of genera to species is 1: 1.97. The ratio of the family to genera is 1: 4.66 and that of the family to species is 1: 9.02. (Vide Tables II and III.)

Table I gives the number of families, genera and species with more than ten genera and species.

TABLE I

Family	*Genera*	*Species*	*Family*	*Genera*	*Species*
Capparaceae	5	**13**	Convolvalaceae	**12**	**45**
Malvaceae	**16**	**53**	Solanaceae	10	24
Tiliaceae	4	**18**	Scrophulariaceae	**15**	**22**
Fabaceae	**39**	**122**	Acanthaceae	**22**	**44**
Caesalpiniaceae	8	**25**	Verbenaceae	**11**	**15**
Mimosaceae	10	**21**	Labiatae	**11**	**22**
Cucurbitaceae	**13**	**23**	Amaranthaceae	10	**18**
Rubiaceae	**14**	**24**	Chenopodiaceae	8	**12**
Asteraceae	**43**	**62**	Euphorbiaceae	**19**	**43**
Apocynaceae	9	**12**	Liliaceae	9	**12**
Asclepiadaceae	**14**	**18**	Cyperaceae	6	**34**
Boraginaceae	4	**13**	Poaceae	**72**	**150**

Of the 129 families 58 have 1 genus, 16 have 2 genera, 14 have 3 genera, 10 have 4 genera, 7 have 5 genera, 1 has 6 and 7 genera each, 3 have 8 genera, 2 have 9 genera and 4 have 10 genera. In the remaining 13 families genera vary from 11 to 72 and these are shown in bold types in table I. Of these 58 families having one genus 36 have one species i.e. monotypic.

Of the 129 families 36 have 1 species, 21 have 2 species, 14 have 3 species, 9 have 4 species, 10 have 5 species, 2 have 6 species, 4 have 7 species, 2 have 8 and 9 species each, and 5 have 10 species There is not a single family with 11 species. In the remaining 24 families species vary from 12–150 making up 73 per cent of total flora and these are also shown in bold types in table I. Thus there are large number of monotypic genera and families.

Of the 602 genera 397 are represented by only 1 species, 94 by 2, 44 by 3, 23 by 4, 11 by 5, 9 by 6, 5 by 7, 4 by 8 and 9 each and 2 by 10 species. In the remaining 9 genera species vary from 11 to 19. These are Cyperus Linn., 19. Ipomoea Linn., 18. Crotalaria Linn., Indigofera Linn. and Euphorbia Linn. 15 each, Hibiscus Linn, and Cassia Linn. 13 each,

Eragrostis Beauv. 12 and Alysicarpus Neck 11. Of these 9 genera 3 belong to Fabaceae, and 1 each to Malvaeae, Caesalpiniaceae, Convolvulaceae, Euphorbiaceae, Cyperaceae and Poaceae.

Except for the families Poaceae, Cyperaceae, Liliaceae, Commelinaceae and Palmaceae the Monocotyledons are very poorly represented. Of the 263 species of Monoaotyledons 216 belong to the above 5 families while the remaining 47 species belong to 19 different families. Except for the families Fabaceae, Asteraceae, Malvaceae, Convolvulaceae, Acanthaceae, Euphorbiaceae, Caesalpiniaceae, Rubiaceae, Solanaceae, Cucurbitaceae, Scrophulariaceae, Labiatae and Mimosaceae, the Dicotyledons are also poorly represented. Of the 922 species of Dicotyledons 530 belong to above 13 families while the remaining 392 species belong to 92 different families.

Comparisons

These can be best seen from the following tables II to V.

TABLE II

	Dicotyledon			*Monocotyledon*		
	No.	*%*	*Year*	*No.*	*%*	*Total*
Family	72	82.76	1910	15	17.24	87
	105	81.39	1966	24	18.61	129
Genera	287	84.91	1910	51	15.09	338
	475	78.85	1966	127	21.15	602
Species	509	85.55	1910	86	14.45	595
	922	77.80	1966	263	22.20	1185

TABLE III

	1910	1966
Ratio of Monocotyledon to Dicotyledon of species	1:5.92	1:3.50
Ratio of Monocotyledon to Dicotyledon of genera	1:5.63	1:3.73
Ratio of Monocotyledon to Dicotyledon of family	1:4.80	1:4.37
Ratio of genera to species	1:1.76	1:1.97
Ratio of family to genera	1:3.88	1:4.66
Ratio of family to species	1:6.88	1:9.02

TABLE IV

1910					1966				
Genera	*Species*	*Place*	*% of Total*	*Family*	*Family*	*Place*	*Genera*	*Species*	*% of Total*
46	124	1	20.67	Leguminosae	Leguminosae	1	57	168	14.17
24	52	2	8.74	Gramineae	Gramineae	2	72	150	12.65
30	37	3	6.22	Compositae	Compositae	3	43	62	5.23
12	31	4	5.21	Malvaceae	Malvaceae	4	19	56	4.72
10	24	5	4.03	Convolvulaceae	Convolvulaceae	5	12	45	3.79
9	24	5	4.03	Euphorbiaceae	Acanthaceae	5	23	45	3.79
13	19	6	3.02	Acanthaceae	Eurphorbiaceae	6	19	43	3.62
11	17	7	2.85	Cucurbitaceae	Cyperaceae	7	6	34	2.87
7	14	8	2.35	Labiatae	Rubiaceae	8	14	24	2.02
3	14	8	2.35	Tiliaceae	Solanaceae	8	10	24	2.02
11	14	8	2.35	Asclepiadaceae					
10	13	9	2.18	Rubiaceae	Cucurbitaceae	9	13	23	1.94
6	13	9	2.18	Boraginaceae					
7	12	10	2.01	Amaranthaceae	Scrophulariaceae	10	15	22	1.86
					Labiatae	10	11	22	1.86
6	10	11	1.68	Capparidaceae	Boraginaceae	11	6	21	1.77
5	8	12	1.32	Solanaceae	Asclepiadaceae	12	16	20	1.68
5	7	13	1.15	Chenopodiaceae	Tiliaceae	13	4	18	1.51
2	7	13	1.15	Cyperaceae	Verbenaceae	13	12	18	1.51
6	7	13	1.15	Liliaceae	Amaranthaceae	13	10	18	1.51
5	6	14	0.98	Scrophulariaceae	Urticaceae	14	9	16	1.35
6	6	14	0.98	Verbenaceae					
2	6	14	0.98	Urticaceae					
6	6	14	0.98	Palmaceae					
2	5	15	0.84	Aizoaceae	Capparidaceae	15	5	13	1.09
4	5	15	0.84	Apocynaceae	Apocynaceae	16	9	12	1.01
					Chenopodiaceae	16	8	12	1.01
					Liliaceae	16	9	12	1.01
					Aizoaceae	17	4	10	0.84
					Palmaceae	17	8	10	0.84
249	481		79.24				414	898	75.67

From table II it is seen that there is increase in the number of families, genera and species of Dicotyledons and Monocotyledons. In the recent survey there is decrease in the percentage of families, genera and species of Dicotyledons while there is increase in the percentage of families, genera and species of Monocotyledons.

From table III it is seen that in the recent survey ratio of Monocotyledon to Dicotyledon of species, genera and family is comparatively low while that of genera to species, family to genera and family to species is comparatively high.

The families having first seventeen place with the number of genera, species and percentage of total are shown in table IV.

From the above table it is seen that Leguminosae, Gramineae, Compositae, Malvaceae, Convolvulaceae, and Urticaceae have maintained their former positions 1st, 2nd, 3rd, 4th, 5th and 14th respectively, though they have received a significant number of additions during the period of last fifty five years. Euphorbiaceae and Acanthaceae have exchanged their 5th and 6th place. Family having high or low rank can be seen from its place number. Further it is remarkable that families having less number of species have higher positions than families having more number of species. These are Euphorbiaceae, Cucurbitaceae, Labiatae, Tiliaceae, Asclepiadaceae, Boraginaceae, Amaranthaceae, Capparidaceae, Chenopodiaceae, Liliaceae, Palmaceae, Aizoaceae (=Ficoideae) and Apocynaceae. Only six families having more number of species have attained higher ranks. These are Acanthaceae, Rubiaceae, Solanaceae, Cyperaceae, Scrophulariaceae, and Verbenaceae. These families though included in first seventeen places, there are more number of families having less number of species have high ranks. So it is not necessary that with the addition of number of species the family would have high rank.

With regard to percentages of these families it is noticed that in the recent survey there is higher percentage for Gramineae, Acanthaceae, Cyperaceae, Solanaceae, Scrophulariaceae, Verbenaceae, and Apocynaceae while there is lower percentage for Leguminosae, Compositae, Malvaceae, Convolvulaceae, Euphorbiaceae, Rubiaceae, Cucurbitaceae, Labiatae, Boraginaceae, Asclepiadaceae, Tiliaceae, Amaranthaceae, Capparidaceae, Chenopodiaceae, Liliaceae, and Palmaceae. Aizoaceae is the only family which

has equal number of percentage 0.84 in both, but the rank differs as 15th in one and 17th in the other. With the exception of Gramineae in one and Compositae in the other there is a gradual fall in the percentage of families. Hence there is not much change in the distribution pattern of dominant families.

Table V gives mean (M), Standard deviation (S.D.), Co-efficient of variations percentage (C.V.) of genera and species and correlation coefficient (CR) of genera to Species for the year 1910 and 1966.

TABLE V

	M		SD		C.V%		CR
Year	*G*	*Sp.*	*G*	*Sp.*	*G*	*Sp.*	*G to Sp.*
1910	3.87	6.85	6.50	15.18	167.90	221.60	0.9477
1966	4.48	9.11	8.64	19.22	192.90	210.90	0.9230

Applying the tests for significance of differences between Means, SDs and Correlation Coefficients of the year 1910 & 1966, it is observed that these differences are insignificant.

Discussion

In the first place it should be noted that Indraji's monamental work relates to Barda mountain and as such cultigens etc. are not included in it; but in the recent survey they are included and it retates to the Saurastra as a whole.

The increase in the number of families is mostly due to the splitting of the families and to some extent a few new additions. They are Magnoliaceae (1, 1), Rosaceae (1, 1), Rhizophoraceae (2, 2), Onagraceae (1, 1), Turneracea (1, 1), Apiaceae (5, 5), Goodeniaceae (1, 1), Lobeliaceae (1, 1), Myrsinaceae (1, 1). Loganiaceae (1, 1), Orobanchaceae (2, 2), Lentibularaceae (1, 3), Lauraceae (1, 1), Santalaceae (1, 1), Lamnaceae (1, 2), Eriocaulaceae (1, 3) and Juncaceae (1, 1). Figures in the brackets represent the number of genera and species.

With regard to increase in the number of genera, a lot of changes have also taken place by breaking up a genus into smaller units according to the present concept of International code of Botanical nomenclature. Besides there are additions of genera of additional families, genera of cultigens, name changes and also of a new records. Mention may be made of few such as Ammannia Linn., Andropogon Linn., Chloris SW., Cyperus Linn., Eugenia Linn., Eleusine Gaertn., Grewia Linn., Hibescus. Linn., Hygrophila R.Br., Ipomoea Linn., Ischaemum Linn., Justicia Linn., Mimusops Linn., Mollugo Linn., Odina Roxb., Oldenlandia Linn., Phyllanthus Linn., Pycreus Beauv., Pithecolobium Mart, Pergularia Linn., Panicum Linn., Ruellia Linn., Saccopetalum Bennelt, Senebiera DC., Stercula Linn., Thespesia Soland., Vinca Linn., Vitis Linn. etc.

Additions in the families, genera and species have jointly resulted in the increase in the number of species with the result that there is a rise in the ratio of genera to species and family to genera and species (Vide table III).

Conclusions

With all these increase in species, genera and families during the lapse of fifty-five years period there is not much change in the distribution pattern of dominant families which is a remarkable feature. Indraji has stated in the preface on page 5 that the account relates to the plants of Porbander State. It shows his modesty but from the above statistics it should be well taken as the representative flora of Saurashtra as a whole.

Summary

In this paper the statistical synopsis of the recent flora of Saurashtra is compiled and then it is compared with the similar synopsis based on " Vanaspati-Shastra " with the result that though there is increase in species, genera and families, the distribution pattern of dominant plants is not changed and it can be taken as the representative flora of Saurashtra as a whole.

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SOME TRIVALENT METAL COMPLEXES OF 2–HYDROXY–5–METHOXY–ACETOPHENONEOXIME

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The ligand 2-hydroxy-5-methoxy acetophenoneoxime (L) is used for studying complex formation behaviour of Fe^{3+}, Mn^{3+} and Cr^{3+} ions. This ligand, L, has been earlier used[1,2] for studying the complexes formed with Cu^{2+} and Ni^{2+}. A similar ligand 2—hydroxy—5—methyl acetophenone-oxime was used recently[3] for Fe^{3+}, Mn^{3+} and Cr^{3+} ions and the present study for the same ions was undertaken to observe the difference in properties of the two types of chelates formed. The ligand, L, was prepared from ketone[4] by means of hydroxylamine hydrochloride.

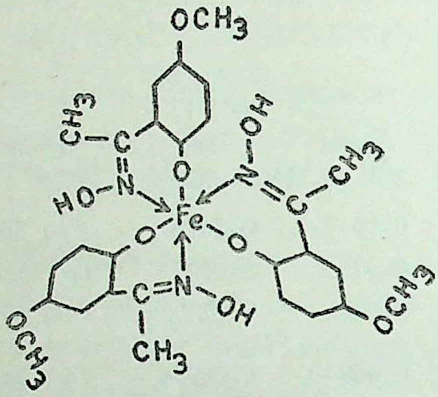
The complexes with the metal ions are precipitated in the pH range 6 to 8 by adding to their trivalent metal chlorides a 2% alcoholic solution of L. The metal chlorides were maintained in excess. The precipitates were digested for an hour and filtered, washed with water to remove excess metal ions and dried. The chelates are coloured : ferric is reddish brown, manganic is brown and chromic is bluish—green. They are all quite stable upto temperature of 150°C., their weights remaining constant on heating upto 150°C. They are completely insoluble in water. The Fe^{3+} and Mn^{3+} chelates are soluble in organic solvents such as benzene, chloroform, CCl_4, etc., and can be recrystallised from them; chloroform is found quite convenient. Chromium chelate, surprisingly, is insoluble in organic solvents. All the three chelates are decomposed by acids and alkalies. Metal analysis, given in the Table I, shows them all to be 1 : 3 complexes. For Fe^{3+} and Mn^{3+} chelates this was confirmed by Job's method by extraction into chloroform and studying the optical density of different solutions. The maxima in the graph of O.D. Vs M / M+L were found, in the two cases, at 25% of M^{3+}. Their molecular weights, determined cryoscopically, showed all the three to be monomeric (see Table I). They are, hence, assigned an octahedral structure.

Table I

	Metal content (gm.)			Mol. wt. (10% chelate in camphor)		
Chelate	*Wt. of complex taken (gms.)*	*Found*	*Expected on 1 : 3 basis*	*Found*	*Expected as a monomer*	*Magnetic moment at 25°C (B.M.)*
	0.7	0.0617	0.0615	(*i*) 567		
CrL_3	0.8	0.0705	0.0702	(*ii*) 584	592	3.69
	1.0	0.088	0.0878	(*iii*) 609		
	0.7	0.06949	0.06934	(*i*) 611		
MnL_3	0.8	0.07406	0.07396	(*ii*) 580	595	5.09
	0.9	0.0833	0.0832	(*iii*) 570		
	0.6	0.0566	0.564	(*i*) 609		
FeL_3	0.7	0.0659	0.0658	(*ii*) 567.1	595.9	5.8
	0.8	0.0753	0.0751	(*iii*) 610.8		

The room temperature (25°C.) magnetic moments (B.M.) are 3.69, 5.09 and 5.8 for tris-chelates of Cr^{3+}, Mn^{3+} and Fe^{3+} respectively. These indicate 3, 4 and 5 unpaired electrons[5]. Hence the Cr^{3+}, Mn^{3+} and Fe^{3+} are high spin octahedral cemplexes. The chromic and ferric chelates have a lower magnetic moment than expected on a "spin-only" value. For Cr^{3+}, such a low value is known[6] and is considered due to a positive spin-orbit coupling constant. The absorption spectra of Fe^{3+} and Mn^{3+} chelates dissolved in chloroform were measured. Both showed strong charge transfer bands which had long tails in the visible. The ligand bands in the visible steal intensity from these charge transfer bands and hence they show unexpected intensity. The Fe^{3+} chelate has a broad band in the visible without any structure in it. This seems to be consistent with a $^6A_{1g}$ ground state, the transition being both Laporte-and spin-forbidden[7]. Some possible very weak spin-forbidden transitions are probably swamped by the charge-transfer spectrum in the vicinity. The Mn^{3+} chelate shows two bands near each other at 720 nm. and 630 nm. The lower ^5E_g state must be splitting, as required by the Jahn-Teller Theorem, giving two,

instead of one, bands[8]. These spectra are thus consistent with an octahedral arrangement of ligands. The specturum of Cr^{3+} complex could not be studied in solution because of its insolubility in the usual solvents.



FeL_3

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SPECTROPHOTOMETRIC STUDY OF COPPER (II) COMPLEX OF 7-NITRO-8-QUINOLINOL-5-SULPHONIC ACID

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7-Nitro-8-quinolinol-5-sulphonic acid (abbreviated as NQSA) was first prepared by J. Molland.[1] Its complexes with iron were studied.[2] Besides iron, only copper(II), amongst all common cations, gives green colour with NQSA. Therefore, formation of Cu(II) complexes was studied spectrophotometrically following all the three well-known methods, viz. (*i*) Job's method,[3] (*ii*) Mole ratio method,[4] (*iii*) Slope ratio method.[5]

The visible spectra of NQSA (5×10^{-3} M) at acidity of 2M HCl, and pH 4 and 12 are given in Fig. 1. Spectra of intermediate pH lie between these curves and are not depicted. From Fig. 1, it is clear that NQSA does not absorb appreciably in the region of 700 to 550 nm. Below 550 nm, absorption increases rapidly. The visible spectra of Cu(II) complex at pH 2 and 8 are depicted in Fig. 2. The spectra at intermediate pH, lie in between above curves. From Fig. 2, it appears that only one charecteristic peak at 625 nm is obtained. Therefore, Job's method at pH 2, 4, 6 and 8 was followed using 625 nm wavelength. (Results are not given.) It was found that maximum occured at 0.33 mole fraction of Cu(II) at all pH indicating that only 1:2 complex is formed. Detailed investigation was carried out following all three methods at pH 5. For absorbance measurements, pH 5.0 was selected because with increase in pH absorbance increased. But above pH 6.0, when Cu(II) is in excess, precipitation of coper hydroxide occurred.

Experimental

Stock 0.05 M solution of $CuSO_4$ and Na_2R (disodium salt of NQSA) were prepared and they were standardized by EDTA and HCl respectively. All chemicals used were of A.R. or G.R. grade. Absorbance measurements were carried out at 625 nm, employing SP 500 Unicam spectrophotometer. As the extinction coefficient of copper complex is low, 4 cm. cuvetts were used for all absorbance measurements. Absorbance measurements were

corrected for either excess of Cu(II) or NQSA, whenever necessary. The colour developed was stable for three days. 5.0 pH was maintained by addition of 5.0 ml. of phthalate buffer.[6] Total volume of all mixtures was kept to 25.0 ml. After absorbance measurements pH of all the mixtures were measured and were found to be 5.0 ± 0.1. No attempt was made to control the temperature. However, the temperature during the measurements remained 32 ± 2^0.

Results and discussion

Job's method of continuous variation was followed using three equimolar concentrations of Cu(II) and Na_2R viz., 0.005, 0.004 and 0.003 M. Results are depicted graphically in Fig. 3. From the figure, it is clear that maxima occured at 0.33 mole fraction of copper in all cases, indicating the formation of 1:2 comple.

Mole ratio method was studied by (A) varying amount of Na_2R and keeping fixed amount of Cu(II) and (B) viceversa. Two equimolar concentrations of Cu(II) and Na_2R viz., 0.005 and 0.004 M, were used for both cases (A) and (B). Results are depicted graphically in Fig. 4 The two linear portions of all the four curves, intersect at composition (5.0 ml. Cu: 10.0 ml. Na_2R) corresponding to 1:2 complex.

The slope ratio method was followed employing one set of concentration of Cu(II) and Na_2R viz., 0.005 and 0.02 M and viceversa. Results are depicted graphically in Fig. 5. The ratio of $slope_1$ and $slope_2$ comes out to be 2.19. The slightly higher value of ratio ot slopes may be due to interference of phtalate ion (added as buffer) which might have lowered absorbance when copper ion is in excess. This tendency of lowering of absorbance reading in the presence of excess of copper ion is apparent from Job's and mole ratio curves. However, when ratio of slopes are taken from the first straight line portion of the mole ratio graphs, (here the mixture are similar to slope ratio method, with only change that proportion of excess Cu(II) or Na_2R is less) it turns out to be 1.93 and 2.00 for 0.005 and 0.004 M solutions respectively. Thus all the three methods indicate the formation of 1:2 complex.

Thanks are due to late Prof. A. M. Trivedi for interest in the work,

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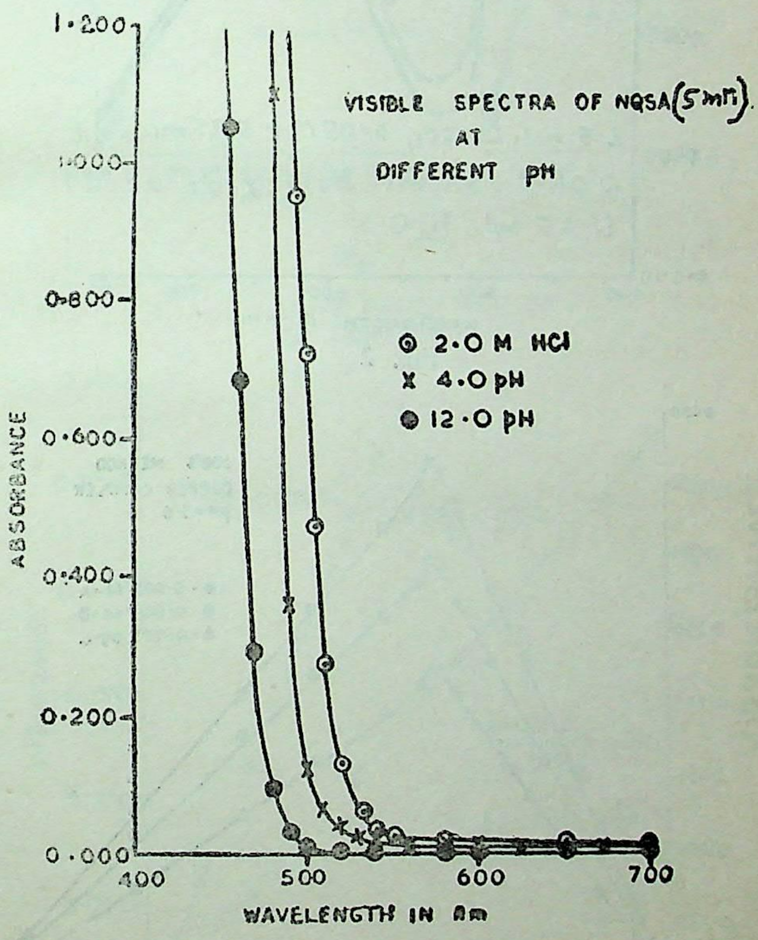
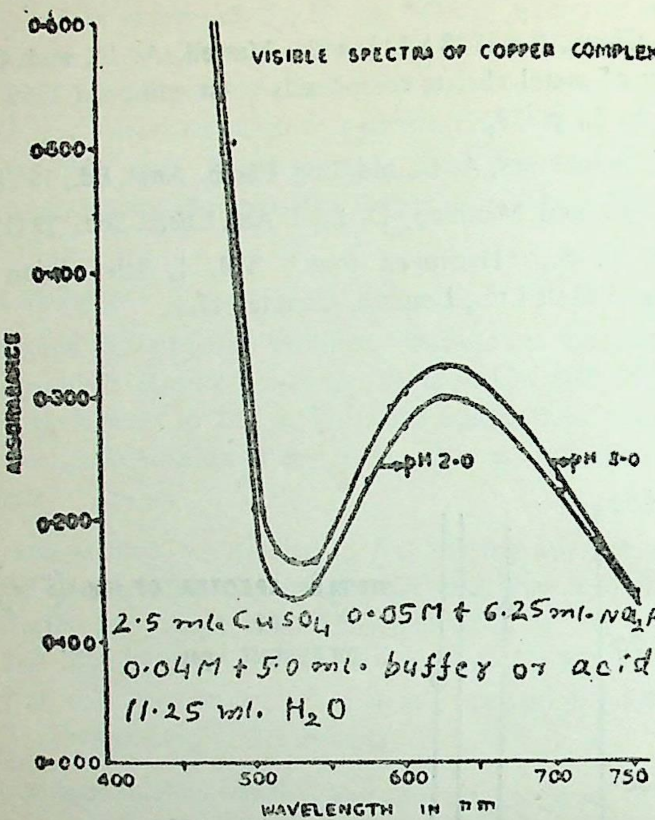
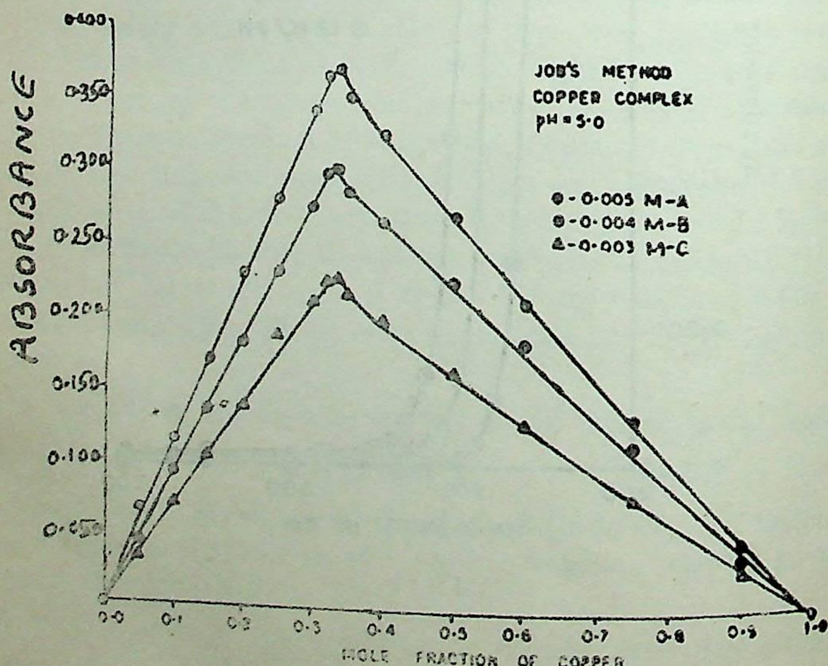


Fig. 1



VISIBLE SPECTRA OF COPPER COMPLEX
ABSORBANCE
pH 2·0
pH 5·0
2·5 ml. CuSO4 0·05 M + 6·25 ml. Na2R 0·04 M + 5·0 ml. buffer or acid + 11·25 ml. H2O
WAVELENGTH IN mμ

Fig. 2



JOB'S METHOD
COPPER COMPLEX
pH = 5·0
0·005 M-A
0·004 M-B
0·003 M-C
ABSORBANCE
MOLE FRACTION OF COPPER

Fig. 3

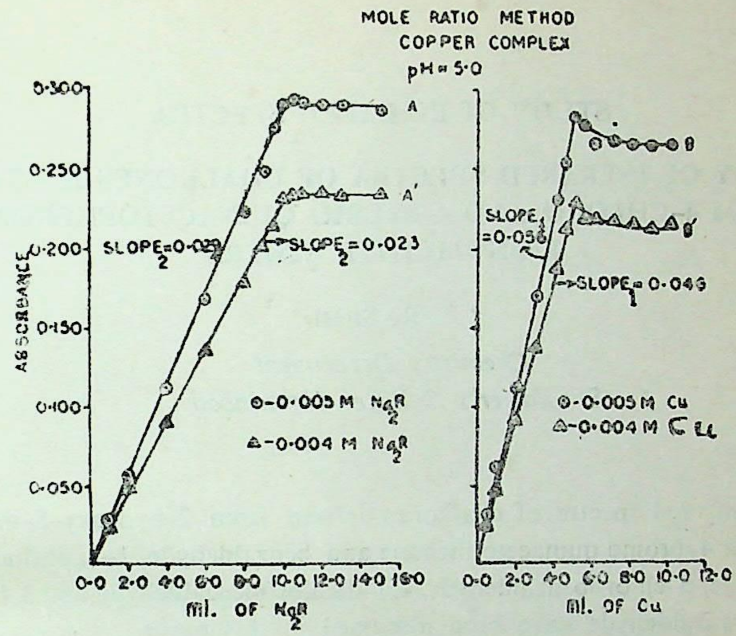

MOLE RATIO METHOD
COPPER COMPLEX
pH = 5·0
ABSORBANCE
SLOPE₂=0·023
SLOPE₁=0·056
SLOPE₁=0·046
○-0·005 M Na₂R
△-0·004 M Na₂R
○-0·005 M Cu
△-0·004 M Cu
Ml. OF Na₂R
Ml. OF Cu

Fig. 4

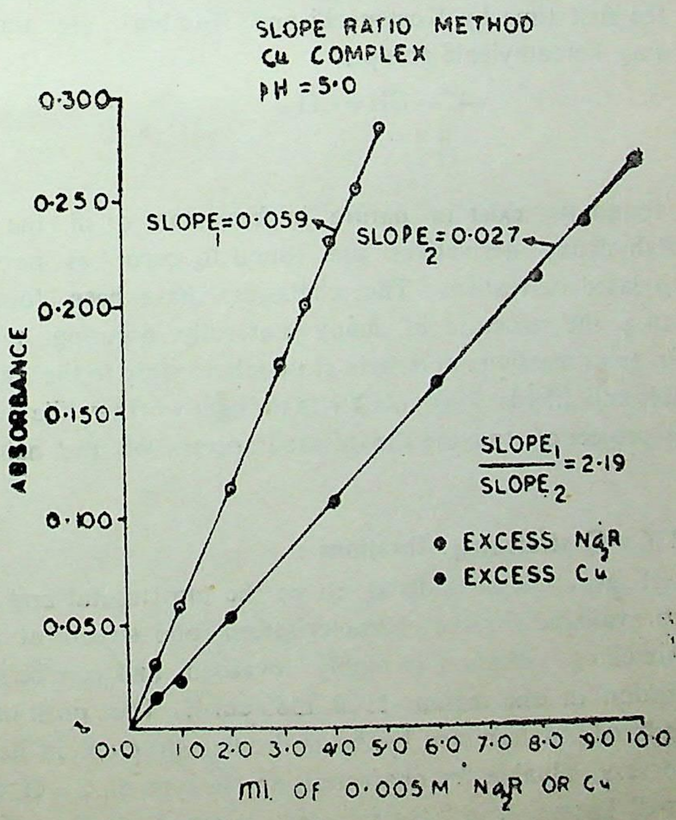

SLOPE RATIO METHOD
Cu COMPLEX
pH = 5·0
ABSORBANCE
SLOPE₁=0·059
SLOPE₂=0·027
SLOPE₁/SLOPE₂=2·19
EXCESS Na₂R
EXCESS Cu
Ml. OF 0·005 M Na₂R OR Cu

Fig. 5

STUDY OF INFRARED SPECTRA

STUDY OF INFRARED SPECTRA OF CHALKONES DERIVED FROM 4-CHLORO AND 4-BROMO QUINACETOPHENONE MONOMETHYL ETHERS

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The infrared spectra of chalkones derived from 2-hydroxy-5-methoxy-4-chloro or 4-bromo quinacetophenone and benzaldehyde, 1-naphthaldehyde, anisaldehyde, p-chlorobenzaldehyde, 2,4-dichlorobenzaldehyde and 3,4-methylenedioxybenzaldehyde have been discussed in this paper.

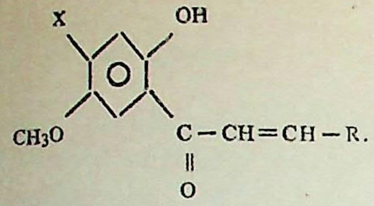
Benzylidene ketone or phenyl-styryl ketones commonly named as chalkones for the first time by Kostanecki and Tambor[1] are unsaturated ketones containing ketoethylenic group :

$$-\underset{\underset{O}{\|}}{C}-CH=CH-$$

They are found to exist in nature in free state or in the form of Glycosides. Polyhydroxy derivatives are found to occur as partially or completely methylated derivatives. The chalkones have been found to be useful for deciding the structure of many naturally occuring substances. In view of their great reactivity and their close relationship to the flavanones, flavones, flavonols and dihydroflavonols it was thought worth-while to undertake the present project of studying the infrared spectra of the halogeneted chalkones[2].

The C=O and C=C stretching vibrations :

The carbonyl group is considered to be the most useful and effective functional group available for the characterisation and structural analysis. The carbonyl stretching vibration is highly localised and can be identified by strong absorption in the region 1900-1580 cm^{-1}. The position of the C=O stretching band is determined by the molecular structure in its vicinity and is therefore very valuable for characterising the type of C=O, carbonyl function. It is well known from the infrared spectral studies of several



R=	X=	C——H^a	—CH_a^b	C===O^c	C===C^d	—Ar—e	—$OCH_3^{f_1}{}_{f_2}$	CH=$CH^{g_1}{}_{g_2}$	-$CH_3^{h_1}{}_{h_2}$	=C-O-$C^{i_1}{}_{i_2}$	C–O^j	C—O^k	C—H^l	C—H^m	C—X^n
—Phenyl	Cl	3030w	2994 2915w 2857	1650s	1580s	1488s	1468s 1453m	1393s 980s	1368s 1176s	1261s 1026s	1200s	1282s 1062s	1134w,1103w, 1053m,1000m,990w	869s,857s,820s 800s,769s,727s	703m
1—Naphthyl	Cl	3067w 3030w	2994 2941w 2907	1650s	1582s	1493s	1475s 1447m	1404m 974s	1364s 1188s	1263s 1026s	1200s	1289s 1062s	1132w,1104w, 1012m,1042w,950w,	859s,852m,833m 794s,768s,721m	702m
P—Methoxy-phenyl	Cl	3021w	2967 2933w 2890	1647s	1585s	1508s	1460s 1425w	1397s 976s	1366m 1176s	1250s 1037s	1198s	1271s 1063s	1149w,1121w, 1106m,970w,952w	865m,854m,830m 813s,800s,761m	704w
P—Chloro-phenyl	Cl	3106w	2967w 2865	1650s	1585s	1488s	1473m 1449w	1410m 981m	1359s 1181s	1250s 1031s	1202s	1277m 1063s	1119w,1106m, 1086m,1017m,970w	777s 862m,823s,811s	707w 744w
2:4—Dichloro-Phenyl	Cl	3195w 3030	2976 2915w 2849	1650s	1582s	1490s	1475s 1447m	1401s 980m	1359s 1176s	1253s 1026s	1199s	1294s 1059s	1152w,1143w, 1104m, 960w,	886m,867s,831s 825s,749s,723s	702m 758w
—Phenyl	Br	3067w	2994 2941w 2874	1650s	1580s	1488s	1471m 1453m	1389m 980m	1368m 1176m	1255s 1031s	1190s	1283s 1046s	1155w,1131w, 1040w,1022m,971w	889m,862m,816s 769s,730s	689m 677w
1—Naphthyl	Br	3086w	2959w 2865	1647s	1580s	1488s	1471m 1445m	1397s 975s	1361s 1174s	1261s 1024s	1200s	1284s 1048m	1124w,1092w, 1014m, 960w	862s,823m,796s 774s,719m	691m
P—Methoxy-phenyl	Br	3049w	2959 2933w 2849	1653s	1565s	1515m	1466m 1449w	1389m 979m	1366m 1174s	1259m 1031m	1200s	1282m 1052m	1114w,1033w,937w	823m,790m 740w	692w
P—Chloro-Phenyl	Br	3096w	2976 2935w 2857	1650s	1567s	1493s	1471m 1447w	1395m 980m	1365s 1176s	1263m 1026m	1198s	1274m 1052s	1116w,1104w, 1088w,1013w,959w	857m,817s,800m 775s,746m	699w
2:4—Dichloro-Phenyl	Br	3096w 3030w	2994 2959w 2874	1650s	1580s	1488s	1471w 1449w	1393s 977m	1359s 1178s	1252s 1021s	1198s	1294s 1045s	1155w,1142w, 1102m, 961w	826s,794s,722m	693m
3:4—Methylene-dioxyphenyl	Br	3086w	3003 2924w 2865	1647s	1575s	1494s	1456vs	1391s 973m	1348m 1178s	1250s 1037s	1200s	1290s 1052s	1124w,1103m, 985w,950w	857m,843m,813s 800s,757m	692m

(a) C——H stretching vibration; (b) Triplet due to —CH_3 symmetrical stretching vibration; (c) C===O stretching vibrations; (d) C===C stretching vibration; (e) Aromatic ring stretching vibration; (f_1) —C CH_3 asymmetric bending vibration; (f_2) —OCH_3 symmetric bending vibration; (g_1) CH===CH:-CH in palne deformation; (g_2) CH===CH: —CH out of plane deformation; (h_1) —CH_3 methyl group; (h_2) —CH_3 Methyl rocking (i_1) =C—O—C antisymmetrical stretching; (i_2) =C—O—C symmetrical stretching; (j) C——O stretching vibration due to —O——H group; (k) C===O skeletal vibrations; (l) C——H in plane deformation due to substitution in benzene ring; (m) C——H out of plane deformation due to substitution in benzene ring; (n) C——Cl or C——Br stretching vibration.

compounds, that conjugation of ethylenic double bonds or of carbonyl group and ethylenic double bond causes a shift from the normal position to a longer wavelength. Thus C=O group in acetone shows a band at 1718 cm^{-1}, while conjugation with one phenyl ring as in acetophenone lowers the frequency to 1687 cm^{-1} and conjugation with two phenyl groups as in benzophenone lowers the frequency to 1655 cm^{-1}. α-β-unsaturated ketones normally give bands in the region 1685-1665 cm^{-1} but conjugation of double bonds with, C=O, carbonyl group results in a low frequency shift of the C=C absorption, which is similar to but smaller than that arising from normal pair of conjugated double bonds. Thus rasmussen et. al[3] place the C=C absorption of isophorone at 1639 cm^{-1} and state that the type of conjugated ketone shows the C=C band falls in the region 1647-1621 cm^{-1}.

In α-β-unsaturated ketones two absorption bands are found in the C=C stretching region and the high frequency band may be assigned to the C=O stretching and the lower frequency band to the C=C stretching vibrations. However if the ketone does not assume the S-transform and is locked in the S-cis from the relative intesities will be reversed[4]. Furthermore it has been noted by braude et. al[5] that the C=O and C=C bands of the S-cis form are shifted respectively to lower and higher frequencies so that the two bands become rather widely separated (by 75 cm^{-1}).

Randall et. al[6] regarded a band in the range 1587-1575 cm^{-1} as a positive indication of conjugation of a double bond with the aromatic ring where a carbonyl group or any unsaturated group is directly attached to the ring, however, the intensity of the second band near 1580 cm^{-1} is considerably enhanced and becomes much more prominent in the spectrum.

Hergert and Kurth[7] have reported that unsubstituted chalkones show a carbonyl band at 1659 cm^{-1} which is due to conjugation with a phenyl group and an aliphatic double bond. They also have stated that the introduction of a hydroxyl group in conjugated chelated ortho position to the carbonyl group lowers the carbonyl frequency to about 1620 cm^{-1}. They have also reported a broad band due to chelated hydroxy group at 3280 cm^{-1} in case of 2′,3, 4-trihydroxy chalkone.

The chalkones under investigation are orthohydroxy chalkones and in our study we have found two bands in the region 1633-1645 cm^{-1}. 1582-1565 cm^{1}. In view of the above discussion the first band we have assigned to C=O stretching vibration and the second band to C=C stretching vibration. It has been also observed that the intensity of the second band near 1582-1565 cm^{-1} is greatly enhanced and is much more prominent due to conjugation of the ethylenic double bond with aromatic ring having a carbonyl group directly attached to it.

It is interesting to note that strong bands other than the C=O stretching vibration have been observed in the region 1294–1046 cm^{-1}, these were characterised as skeletal vibrations of the C=O group[8].

The study of the spectra also indicate that the ortho hydroxy group in the chalkone is strongly chelated with the carbonyl group and give a broad band in the region near 2700 cm^{-1}. The low frequency of the C=O stretching band also supports the chelation of the hydroxy group.

The C=C and the C—H stretching vibrations due to aromatic ring :

The fundamental studies in benzene vibrations have shown that the C=C stretching vibrations of the three double bonds around the ring result in resonance splitting effect on the absorption bands produced near 1600 and 1500 cm^{-1}. These bands are highly characteristic of the aromatic ring itself and taken in conjugation with the C—H stretching bands near 3030 cm^{-1} according to Cloth up[9] and with A.P.I. spectra-another C=C stretching band due to aromatic ring is observed near 1525–1475 cm^{-1} depending upon the position of substituents in the ring. Generally it is found near 1500 cm^{-1}, except where para substitution or unsymmetrical trisubstitution causes a shift towards higher frequency or vicinal trisubstitution a shift towards lower frequency. In our investigation we also find a strong band in the region 1515–1486 cm^{-1} which is due to the presence of C=C stretching vibration of the aromatic ring. The C—H stretching band due to aromatic ring is found in the region 3100–3000 cm^{-1}.

The vibrations due to the presence of a methoxy-OCH_3 groups :

As the chalkones under investigation are methoxy chalkones a triplet of aromatic OCH_3 group is found in the region 3000–2850 cm^{-1}. The presence of OCH_3 group is also confirmed by the asymmetric stretching vibrations due to =C—O—C group near 1263–1250 cm^{-1}, as well as symmetric stretching vibrations due to =C—O—C group near 1040–1020 cm^{-1}. These chalkones also show a band due to —CH_3 group near 1370 cm^{-1} and another band due to Methyl rocking near 1180 cm^{-1}.

The C—O Stretching band due to C—OH Group :

A strong band in all the chalkones due to C—O stretching vibration is observed near 1200 cm^{-1}.

The C—H in plane and out of plane deformation :

A number of weak bands in the region 1225–950 cm^{-1} due to C–H in plane deformations vibrutions have been noted indicating the presence of substituents in the phenyl ring. Intense absorption bands are found in the region 950–700 cm^{-1} due to the C—H out of plane deformation vibrations.

All these frequencies and other characteristic vibrations are tabulated in the attached table.

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CONDUCTOMETRIC STUDIES OF METAL-DIETHYL-DITHIOCARBAMATES

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Abstract

In the present work, an attempt has been made to arrive at the formula of some metal diethyldithiocarbamates, conductometrically. The formulas obtained were AgDDC, $Pb(DDC)_2$, $Zn(DDC)_2$ & $Cd(DDC)_2$ where DDC^- is the diethyldithiocarbamate ion. The order of the stability was found to be Ag > Pb > Cd > Zn.

—o—

One of the methods of studying the nature of the complexes is to perform conductometric titrations. The general development of Job's method by the use of any measurable characteristic for the study of complexes has been described by Siddhanta.[1] The application of Job's method of continuous variation of molar conductance was made by Purkaystha[2] and others.[3]

If a complex RA^{m-n} is formed in the solution according to the scheme

$$R^{m+} + A^{n-} \rightleftharpoons RA^{m-n}$$

then the conductivity of the mixture will be less than that which would be observed in the absence of complex formation. The electrical conductivity method has not been applied to systems in which several complexes are formed.

In the present case, formula of silver, lead, cadmium and zinc diethyl-dithiocarbamates were determined. As these complexes were insoluble in water, the conductance was measured in 75% ethanol. The conductivity water of specific conductivity 3×10^{-6} mhos/cm. was used. The resistance of different solutions prepared was measured at 35° ± 0.1°C, with Mullard

conductivity meter. Results are given in Tables 1 to 4. The data obtained are summarised as follows :

No.	*Cation*	*NaDDC*	*Conductance at point of intersection mhos* $\times 10^4$	*Formula of the complex Cation : NaDDC*
1.	1.0 ml $AgNO_3$ 0.001 M	1 ml. NaDDC 0.001 M	0.155	1 : 1
2.	0.7 ml. $Pb(NO_3)_2$ 0.001 M	1.4 ml. NaDDC 0.001 M	0.200	1 : 2
3.	0.8 ml. $Cd(SO_4)_2$ 0.001 M	1.6 ml. NaDDC 0.001 M	0.210	1 : 2
4.	0.8 ml. $ZnSO_4$ 0.001 M	1.6 ml. NaDDC 0.001 M	0.248	1 : 2

Thus the formula of the different complexes are Ag(DDC), $Pb(DDC)_2$, $Cd(DDC)_2$ and $Zn(DDC)_2$.

The conductance of any solution will be due to all the conducting ions present. It is also governed by the nature of the solvent. In the present case, the solvent is 75%, ethanol. At the point of intersection, the conductance will be due to (*a*) conductance of the electrolyte formed during the reaction and (*b*) conductance of the ions obtained from the dissociation of the complex. For example, when NaDDC is added to $AgNO_3$ in the system containing 75% ethanol, the point of intersection obtained corresponds to 1.0 ml. $AgNO_3$ 0.001 M plus 1.0 ml. NaDDC 0.001 M. The following reaction takes place :

$$AgNO_3 + NaDDC \rightarrow AgDDC + NaNO_3$$

Thus at the point of intersection 0.001 M AgDDC and 0.001 M $NaNO_3$ will be formed. Knowing the cell constant, the specific conductance at the point of intersection can be determined. If the specific conductance of $NaNO_3$ is deducted, the specific conductance of AgDDC may be obtained. However, if we assume that the conductance of different salts ($NaNO_3$ or Na_2SO_4) formed in addition to the complex, is almost the same, we may have very roughly the order of stability of the complexes. As we know, less the stability, greater the dissociation, and hence, more the conductivity. Therefore, the increasing order of stability of different complexes will be the same as the decreasing order of conductivity. In the present case the conductance (mhos/cm.) at the point of intersection for different complexes is as follows :

$$AgDDC = 0.155 \times 10^{-4};\ Pb(DDC)_4 = 0.200 \times 10^{-4};$$
$$Cd(DDC)_2 = 0.210 \times 10^{-4};\ Zn(DDC)_2 = 0.248 \times 10^{-4}$$

From the above, the order of conductivity will be as follows :

$$Zn(DDC)_2 > Cd(DDC)_2 \geqslant Pb(DDC)_2 \geqslant AgDDC$$

Hence, the order of stability of different complexes will be as follows :

$$Ag \geqslant Pb > Cd > Zn.$$

TABLE 1

No.	ml. of 0.001 M $AgNO_3$	ml. of 0.001 M NaDDC	ml. of H_2O	ml. of ethanol	1/R mhos × 10^4
1.	0.0	2.0	3.0	15.0	0.290
2.	0.2	1.8	3.0	15.0	0.255
3.	0.4	1.6	3.0	15.0	0.232
4.	0.6	1.4	3.0	15.0	0.210
5.	0.8	1.2	3.0	15.0	0.185
6.	0.9	1.1	3.0	15.0	0.160
7.	1.0	1.0	3.0	15.0	0.155
8.	1.2	0.8	3.0	15.0	0.158
9.	1.4	0.6	3.0	15.0	0.172
10.	1.6	0.4	3.0	15.0	0.198
11.	1.8	0.2	3.0	15.0	0.220
12.	2.0	0.0	3.0	15.0	0.245

TABLE 2

No.	ml. of 0.001 M $Pb(NO_3)_2$	ml. of 0.001 M NaDDC	ml. of H_2O	ml. of ethanol	1/R mhos × 10^4
1.	0.0	2.1	2.9	15.0	0.286
2.	0.2	1.9	2.9	15.0	0.264
3.	0.4	1.7	2.9	15.0	0.248
4.	0.5	1.6	2.9	14.0	0.238
5.	0.6	1.5	2.9	15.0	0.230
6.	0.7	1.4	2.9	15.0	0.200
7.	0.8	1.3	2.9	15.0	0.220
8.	1.0	1.1	2.9	15.0	0.242
9.	1.2	0.9	2.9	15.0	0.272
10.	1.5	0.6	2.9	15.0	0.340
11.	1.8	0.3	2.9	15.0	0.422
12.	2.1	0.0	2.9	15.0	0.498

TABLE 3

No.	ml. of 0.001 M $CdSO_4$	ml. of 0.001 M NaDDC	ml. of H_2O	ml of ethanol	$1/R$ mhos $\times 10^4$
1.	0.0	2.4	2.6	15.0	0.310
2.	0.2	2.2	2.6	15.0	0.298
3.	0.4	2.0	2.6	15.0	0.265
4.	0.6	1.8	2.6	15.0	0.240
5.	0.7	1.7	2.6	15.0	0.220
6.	0.8	1.6	2.6	15.0	0.210
7.	0.9	1.5	2.6	15.0	0.200
8.	1.0	1.4	2.6	15.0	0.200
9.	1.2	1.2	2.6	15.0	0.180
10.	1.5	0.9	2.6	15.0	0.160
11.	1.8	0.6	2.6	15.0	0.142
12.	2.4	0.0	2.6	15.0	0.100

TABLE 4

No.	ml. of 0.001 M $ZnSO_4$	ml. of 0.001 M NaDDC	ml. of H_2O	ml. of ethanol	$1/R$ mhos $\times 10^4$
1.	0.0	2.4	2.6	15.0	0.322
2.	0.2	2.2	2.6	15.0	0.310
3.	0.4	2.0	2.6	15.0	0.292
4.	0.6	1.8	2.6	15.0	0.270
5.	0·7	1.7	2.6	15.0	0.250
6.	0.8	1.6	2.6	15.0	0.248
7.	0.9	1.5	2.6	15.0	0.248
8.	1.0	1.4	2.6	15.0	0.240
9.	1.2	1.2	2.6	15.0	0.238
10.	1.4	1.0	2.6	15.0	0.220
11.	1.8	0.6	2.6	15.0	0.178
12.	2.4	0.0	2.6	15.0	0.110

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TRANSITION METAL CHELATES WITH SCHIFF BASES

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Abstract

The Schiff base formed by the ketone 2–OH, 5–CH_3 acetophenone on condensation with ethylenediamine has been used here to study the chelates formed by it with Cu^{2+}, Co^{2+}, Ni^{2+} and Fe^{2+} ions. Analytical, magnetic and spectral properties of these chelates have been studied and structures assigned to them. Iodo-and pyridine complexes formed by the Ni^{2+}-chelate were also isolated and studied.

* * *

Much research work is being done on the analytical and structural aspects of metal chelates of Schiff bases.[1,2] It was decided to study the complexes of Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{2+} with the Schiff base formed by condensing 2–OH, 5–CH_3 acetophenone with **en.**

Preparation :

The Schiff base 2–OH, 5–CH_3 acetophenone ethylenediamine (L) was prepared by condensing the ketone (2 moles) with the amine (one mole) in presence of absolute alcohol by refluxing the mixture for one hour. The yellow Schiff base formed was recrystallised from alcohol when it showed a m.pt. of 201°c. The metal chelates were prepared by refluxing in alcohol an excess of the corresponding metal salt and the Schiff base (L) for about an hour. Since the chelates are insoluble in water it is found very convenient to maintain, during preparation, an excess of metal salt which can be later washed out with water. The chelate is formed in alcohol and is dropped into water when it precipitates out. Analar $CuSO_4$,

$NiSO_4$, $Co(NO_3)_2$ and $FeSO_4$ were used. The coloured chelates formed were washed with water and recrystallised from chloroform and dried under vacuum. For the preparation of the Co^{2+} and Fe^{2+} chelates, an atmosphere of hydrogen gas was maintained. These four chelates were found to be soluble in organic solvents such as chloroform, benzene, absolute alcohol, carbon tetrachloride, etc. Co^{2+} and Fe^{2+} chelates slowly get oxidised in solution. Solids are quite stable in air upto 150°c. Chemical analysis of the metal showed all of them to be 1 : 1 chelates, i.e., they could be represented as ML where $M = Cu^{2+}$, Ni^{2+}, Co^{2+} or Fe^{2+}. The ligand (L) behaves as a tetradentate one as expected from its formula.

The results are tabulated below :

Mol. wt. Data

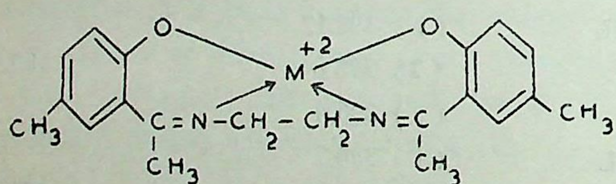
Chelates	*Found*	*Expected for a monomer*
(1) CuL	(1) 390.2	
	(2) 394.7	385.54
	(3) 386.1	
(2) NiL	(1) 392.8	
	(2) 381.0	380.71
	(3) 387.5	
(3) CoL	(1) 398.12	
	(2) 395.8	380.90
	(3) 396.4	
(4) FeL	(1) 380.7	
	(2) 383.4	377.847
	(3) 392.31	
(5) NiL. I	(1) 515.23	
	(2) 520.13	507.6144
	(3) 512.24	
(6) NiL I (py)	(1) 593.28	
	(2) 598.2	586.6211
	(3) 590.93	
(7) NiL $(py)_2$	(1) 555.22	
	(2) 541.33	538.7234
	(3) 543.21	

The iodo-complex of nickel chelate was formed by refluxing the latter, NiL, with iodine in CCl_4 for an hour. On cooling, dark crystals, which analysed as NiL. I were obtained. They were washed with cold CCl_4 in which both NiL and I_2 are soluble but not NiL. I. Similarly, the dipyridinated complex NiL. Py_2 was prepared by refluxing NiL and pyridine in CCl_4 solution for an hour and cooling. NiL. Py_2 was purified by washing it with acetone. Finally NiL. Py. I was prepared by refluxing NiL. I with pyridine for an hour, cooling the mixture, filtering the solid and washing it in turn with CCl_4 and acetone.

Structures :

Chemical analysis showed them to be 1 : 1 complexes. Job's method, applied to solutions of these complexes in $CHCl_3$, confirmed that they were all 1 : 1 complexes as the maxima were always at 50% M/M+L. The molecular weights of these chelates were determined cryoscopically using camphor as a solvent.

It can be seen from the table that they all are monomers. They all showed nearly zero conductivity in nitrobenzene proving the non-electrolytic nature of the chelates. The chelates, therefore, are given the following structure :



Where $M^{+2} = Cu^{+2}, Ni^{+2}, Co^{+2}, Fe^{2+}$.

The magnetic moments of the chelates were determined at room temp., on a Guoy balance. These and other data are given in the Table of Constants given on page 191.

On the basis of the values for the magnetic moments, the number of unpaired electrons in each case is calculated on the "spin-only" basis[3]. Hence are made the tentative assignments of structure. The electronic spectra taken on Beckman DU Spectrophotometer, in $CHCl_3$ for the ML chelates, and in pyridine for the others, are consistent with the structural assignments made. Thus the CuL chelate shows two weak bands at 660 nm

Table of Constants

Sr. No.	Complex ($L=C_{20}H_{22}N_2O_4$)	Metal estimation		Halogen estimation		μ eff	Structure assigned
		Found %	Calculated % on 1:1 Basis	Found %	Calculated % on 1:1 Basis	(B.M.)	
1.	CuL (rosy-red)	16.23	16.36			1.7223 (n=1)	Planar
2.	NiL (reddish orange)	15.35	15.42			diam. (n=0)	Planar
3.	CoL (red)	15.21	15.47			4.023 (n=3)	Tetrahedral
4.	FeL (orange-brown)	14.68	14.79			4.6926 (n=4)	Octahedral
5.	NiL. $(py)_2$ (yellow orange)	11.02	10.91			dia. (n=0)	Octahedral
6.	NiL.I (green)	11.58	11.57	25.12	25.00	1.803 (n=1)	Square pyramidal
7.	NiL. I. (py) (yellowish green)	10.22	10.18	22.14	22.01	1.692 (n=1)	Octahedral

(shoulder) and at 545 nm with a strong charge transfer band at 422 nm. The weak bands can be correlated[4] with the transitions $^2A_{1g} \leftarrow {}^2B_{1g}$ and $^2E_{1g} \leftarrow {}^2B_{1g}$. NiL shows two weak bands : one at 750 nm and the other at 560 nm can be assigned[5] to the electronic transitions $^1B_{1g} \leftarrow {}^1A_{1g}$ and $^1E_g \leftarrow {}^1A_{1g}$. There is a shoulder at 460 nm (medium) and an intense band at 421 nm. The latter is a charge transfer band while the band at 460 nm could be the $n \rightarrow \pi^*$ band of the ligand itself. The CoL shows two weak bands, one band at 560 nm and another at 490 nm with a charge transfer band at 415 nm. The two weak bands can be attributed[6] to the transitions : $^4T_1(F) \leftarrow {}^4A_2$ and $^4T_1(P) \leftarrow {}^5A_2$.

The FeL complex shows two weak bands which are very near each other : One at 500 nm and the other at 438 nm. These seem to be arising from an Jahn-Teller splitting of the transition[7] $^5T_2 \leftarrow {}^5E$. There is also a strong charge transfer band at 390 nm.

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STUDY OF Fe^{3+} AND Co^{3+} CHELATES WITH 2.5-DIHYDROXY ACETOPHENONOXIME

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Abstract

The metal chelates of the ions Fe^{3+} and Co^{3+}, with the ligand 2 : 5-dihydroxy acetophenone oxime, have been studied. The complexes were found to possess 1 : 3 stoichiometry on the basis of analytical & molecular wt. determinations. Magnetic moments show the Fe^{3+} and Co^{3+} complexes to be octahedral.

* * *

Metal chelates formed by 2, 5-dihydroxy acetophenone oxime have been studied for analytical and structural purposes[1] for Cu^{2+}, Ni^{2+} and Pd^{2+} ions. Here it was decided to study the structures of the ferric and cobaltic chelates of this ligand.

Preparation :

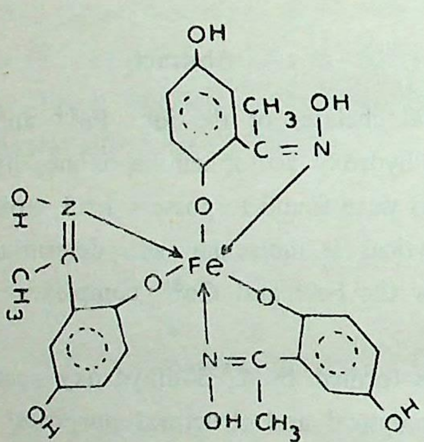
The acetophenone oxime, (L), was prepared by condensing the ketone 2, 5-OH, acetophenone with hydroxylamine hydrochloride by keeping the mixture overnight. The black-red oxime was recrystallised from alcohol.

For the preparation of the complexes, sodium salt of the ligand and proper metal salt solution were refluxed, in presence of acetate buffer, for 1½ hours at pH=6-7. The blackish chelates formed were washed with water and finally with alcohol and dried at 110°-115°c. The complexes are not soluble in any organic solvent. They are stable in air. The chemical analysis showed them to be 1 : 3 in composition, i.e. ML_3. This stoichiometry was confirmed by molecular wt. determination, done cryoscopically, in camphor. It shows them to be monomers.

Mol. wt. Data

No.	*Chelates*	*Expected for a monomer*	*Found*
1.	FeL_3	554	(*i*) 563.0 (*ii*) 560.7
2.	CoL_3	557	(*i*) 564.3 (*ii*) 569.1

The ligand, thus, behaves as a bidentate one as expected. The ferric chelate, therefore, is given the following structure :



The magnetic susceptibilities of complexes were determined at room temp. on a Guoy balance. The magnetic moments were found to be as follows :

μ_{eff} $(FeL_3)=5.88$ B.M.

μ_{eff} $(CoL_3)=3.788$ B.M.

Ferric chelate :

The magnetic moment suggests that it contains five unpaired electrons which indicates a spin-free, outer orbital, octahedral complex.

The absorption spectrum in the visible region was determined on Hungary Spectromon Spectrophotometer. It showed ill-defined curves with high ϵ with no distinct maxima. The charge transfer spectrum of the ligand system has a long tail into the visible and no conclusions could be derived from the study of this spectrum. Further, since the ground state would be a

spin sextet ($^6A_{1g}$) with no other sextet state as a higher level, the absorption bands will be not only Laporte–forbidden but spin–forbidden as well. Hence they are expected to be very weak and are most likely swamped by the tail of the charge–transfer band.

Cobaltic chelate :

The magnetic moment (μ_{eff}=3.79 B.M.) does not provide any unequivocal indication of the number of unpaired electrons in the complex. Two possible explanations can be given and it is difficult to distinguish between the two :

(1) There could be an equilibrium between a spin-free (μ=4.83 B.M.) and a spin-paired (μ=0 B.M.) Co^{3+} complex[2, 3].

(2) The cobaltic state might have got reduced by the ligand system so that what we are handling is a mixture of cobaltous (μ=3.9 B.M.) and cobaltic (μ=0 B.M.) complexes, with the cobaltous prepondering.

The absorption spectrum is, again, similar to the ferric one and is quite indistinct without any clear maxima. The tail of the charge transfer spectrum goes much into the visible, thereby lifting the entire spectrum in the visible region to more than ϵ=800.

We thank Dr. P. K. Bhattacharya, Chem. Dept., M. S. University, Baroda, for permitting us to use the Guoy balance and the Spectrophotometer.

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Cu^{2+}, Ni^{2+} and Co^{2+} COMPLEXES WITH 2-OH-3-Br-5-CH_3 BENZOPHENONEOXIME

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Abstract

The chelates of Cu^{2+}, Ni^{2+} and Co^{2+} with the ligand 2-OH-3-Br-5-CH_3 benzophenoneoxime (L) are prepared. Their analytical, magnetic and spectral characteratics are studied and structural inferences made for the three chelates. It is found that they all can be represented as ML_2 and that while the chelates of Cu^{2+} and Ni^{2+} are square planar, the Co^{2+} chelate is tetrahedral.

* * *

Preparation of the ligand : The ketone, 2-OH-5-CH_3 benzophenone was obtained by Fries migration of p-cresyl benzoate[1]. It was next brominated in acetic acid solution. The bromoketone was then converted into its oxime (L) by treatment with hydroxylamine hydrochloride[2] in alcohol. Recrystallised from alcohol, its m.pt. was 158°C.

Preporation of the chelates : The metal sulphates were refluxed with the ligand in an acetate buffer of PH=6 to 7 for some two hours. The precipitated solid chelates were washed with water and finally recrystallised from chloroform. The copper chelate is dirty-brown, the nickel one is greenish and the cobalt one is yellow. The chelates are insoluble in water, sparingly soluble in alcohol and soluble in chloroform and benzene. They are quite stable upto a temp. of 150°C.

Analysis of chelates : The chelates were broken by a small quantity of nitric acid. The metal content in each case was determined by standard analytical methods. Bromine in each case was estimated by the method of Kay and Haywoods[3]. The metal and bromine contents showed that the

TABLE I

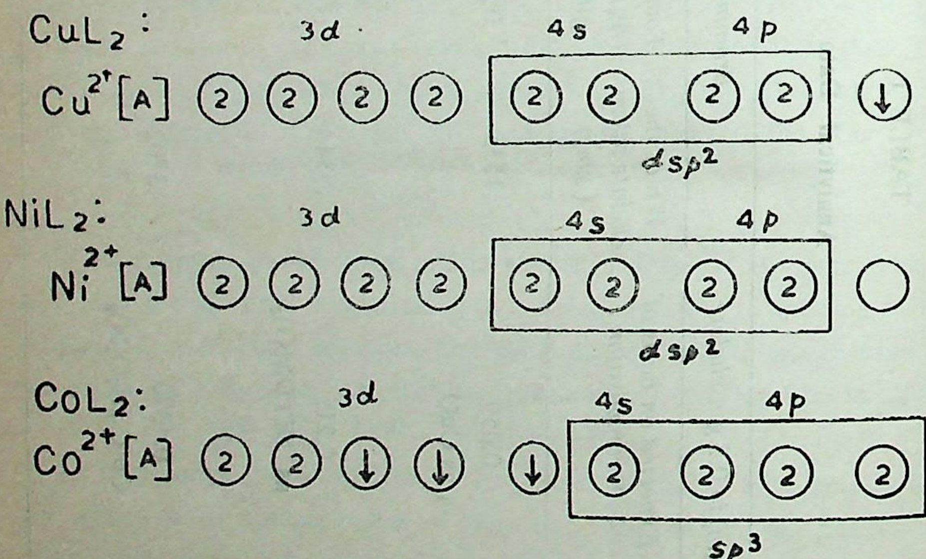
Analytical Data

Chelate	Metal Content (gm) in 0.5 gm chelate: Found	Metal Content: Expected on basis of 1:2 composition	Bromine content: Wt. of the chelate taken (gm)	Bromine content: Found (AgBr) gm	Bromine content: AgBr(gm) Expected on basis of 1:2 Composition	Mol. wt.: Found	Mol. wt.: Expected For a monomer
CuL_2	1. 0.0596 2. 0.0613 3. 0.0610	0.059 (as CuO)	.1535	.090	0.0860	1. 643 2. 660 3. 658	673.5
NiL_2	1. 0.211 2. 0.212 3. 0.211	0.215 as Ni $(DMG)_2$	.3344	.183	0.182	1. 629 2. 650 3. 658	668.7
CoL_2	1. 0.4282 2. 0.4289 3. 0.4351	0.4320 $Co(C_{10}H_7O_2N)_3$	.3702	.205	0.205	1. 638 2. 670 3. 652	668.9

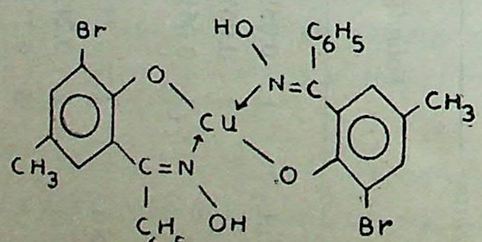
complexes were 1 : 2 in composition. The details of the analysis are given in Table 1. The mol. wts., determined cryoscopically using camphor as the solvent, showed the chelates to be monomeric, i.e., the chelates could be represented as ML_2. The 1 : 2 stoichiometry is confirmed by Job's method of continuous variation. For this, the chelates were extracted in chloroform and the optical densities of solutions of different metal contents were determined. In each case, the maximum was found to be at 33 % of M/M+L giving a 1 : 2 composition for the chelate.

Magnetic properties :

The magnetic susceptibilities of the three chelates were determined at room temperature on a Guoy balance. The magnetic moments calculated from the susceptibilities are found to be 1.9, 0 and 3.9, B. M. for the copper, nickel and cobalt chelate, respectively. On the basis of "spin-only" value, the chelates are assigned one, zero and three unpaired electrons for CuL_2, NiL_2 and CoL_2 respectively. From the number of unpaired electrons, their structures are considered to be square-planar for CuL_2, NiL_2 and tetrahedral for CoL_2. This can be explained on the Pauling's diagrams as follows :



The CuL_2 can be depicted as :



CuL_2 : Square planar; trans-arrangement.

Electronic Spectra :

The visible and the ultraviolet spectra were mapped using solutions of these chelates in chloroform. They were measured on Spectronic 20. The absorption maxima and their extinction coefficients are listed in Table II :

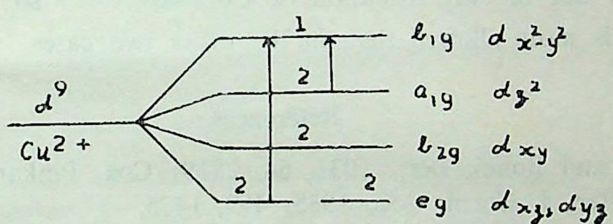
TABLE II

Electronic Spectra and Magnetic Moments

Chelate	*Maxima (nm)*	ε	μ_{eff} (*B.M.*) *at* 25°*C*
CuL_2	660	128	1.8
	470	370	
	385	5200	
NiL_2	610	122	0.0
	480	200	
	400	5600	
CoL_2	650	44	3.9
	540	440	
	380	16000	

These spectra are consistent with the structures assigned. They can be correlated with the crystal field diagrams as shown below :

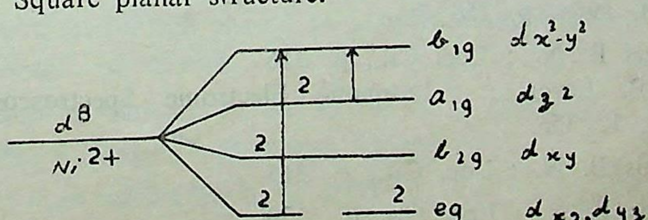
CuL_2 : Square planar structure.



Splitting in an idealised D_{4h} symmetry[6].

The band at 660 nm ($\varepsilon=128$) could be due to the transition $a^2_{1g}\ b^1_{1g}\rightarrow a^1_{1g} b^2_{1g}$ i.e. $^2A_{1g}\leftarrow{}^2B_{1g}$ and the other weak band found at 470 nm (370) may be assigned to the electronic transition $e_g^4\ b_{1g}^1\rightarrow e_g^3\ b_{1g}^2$ i.e. $^2E_g\leftarrow{}^2B_{1g}$. The moderately strong band at 385 nm (5200) is obviously a charge transfer band.

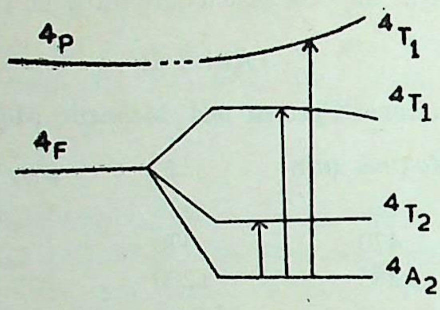
NiL_2 : Square planar structure.



The band[7] at 610 nm (122) may be the $a^2_{1g}\rightarrow a^1_{1g}\ b^1_{1g}$ and the

one at 480 nm (200) the $e_g^4 \rightarrow e_g^3 b_{1g}^1$. The band at 400 nm (5600) must be a charge transfer band.

CoL_2 : Tetrahedral structure



Splitting in a T_d field for a d^7 case (Co^{2+})

The band at 650 nm (44) and 540 nm (440) could be ${}^4T_2 \leftarrow {}^4A_2$ and ${}^4T_1(F) \leftarrow {}^4A_2$ respectively. The latter is a shoulder on the strong band at 380 nm (16000) and hence is rather more intense than expected. The third expected band ${}^4T_1(p) \leftarrow {}^4A_2$ seems to be swamped by the intense charge transfer band at 380 nm. The latter is much more intense than the corresponding bands at 385 nm. and 400 nm. in CuL_2 and NiL_2. It is probably due to easy oxidation of Co^{2+} to Co^{3+} so that the transfer of charge is more allowed than in the other two cases.

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